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DIVISION OF RUBBER CHEMISTRY
of the
AMERICAN CHEMICAL SOCIETY

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RUBBER CHEMISTRY AND TECHNOLOGY

Rubber Chemistry and Technology is published quarterly under the supervision of the Editor representing the Division of Rubber Chemistry of the American Chemical Society. The object of the publication is to render available in convenient form under one cover all important and permanently valuable papers on fundamental research, technical developments, and chemical engineering problems relating to rubber or its allied substances.

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NEW BOOKS AND OTHER PUBLICATIONS

RUBBER RED BOOK. 1943 Edition. Fourth issue. Published by *The Rubber Age*, 250 W. 57th St., New York 19, N. Y. Cloth. 6 x 9 inches. 580 pages. Price $5.00.—As indicated by statements of the editor and of the publisher in the beginning of the book, this directory of the rubber industry, issued biennially, was prepared under more difficult and different conditions than editions of previous years. Despite these more exacting conditions, this latest issue represents a commendable effort to review and bring up to date information of value to those both in and out of the industry. Containing about 70 more pages than did the 1941 edition, the 1943 edition follows about the same system of organization and classification. An article entitled, "Place of the Reclaiming Industry in the War Effort", by M. G. Shepard, Development Manager, Naugatuck Chemical Division, United States Rubber Co., presents a summary of happenings in the reclaiming industry during the past two years and progress on the problems of this section of the rubber industry. Rubber companies whose activities have been temporarily suspended until the supply and restriction situation becomes more satisfactory are footnoted to explain this fact. The 1943 edition contains sections on the following: rubber manufacturers in the United States, classified alphabetically according to products, and geographically; rubber manufacturers in Canada; rubber machinery and equipment, listed by types and with manufacturers' names and addresses; accessories and fittings listed in a similar manner; rubber chemicals and compounding materials, listed as to type, and as to trade and brand names and including suppliers' addresses; fabric and textiles; crude rubber and related materials; synthetic rubber and other rubberlike materials; reclaimed rubber; scrap rubber dealers; rubber derivatives; rubber latex, including water dispersions and special latex processes, compounding materials and machinery and equipment; miscellaneous products and services, with new listings on fireproofing of fabrics, mildew treatment, processed separator cloth, etc.; consulting technologists; manufacturers' representatives, sales agents, branch offices, etc. in the United States and Canada; technical journals; trade and

technical organizations; and "Who's Who in the Rubber Industry". A subject index is also included. The book, which contains and correlates an extensive amount of data on the present-day rubber industry, should be of increased value during the war and the transition period. [From the *India Rubber World.*]

ANNUAL REPORT ON THE PROGRESS OF RUBBER TECHNOLOGY: 1942. Edited by T. J. Drakeley. Published by the Institution of the Rubber Industry, 12 Whitehall, London, S.W. 1, England. 7½ x 9¾ in. 131 pp. Price to members, 2/6 (approximately 60c); To nonmembers, 10/6 (approximately $2.50).—Once again the Institution of the Rubber Industry has succeeded in compiling an annual report, despite all the difficulties these days in such compilation. Although the report covers 1942 and has been considerably delayed, the data are of extreme value to chemists and technologists. The current report follows previous editions in scope, which embraces all branches of the rubber industry. The compilation of specific reports is entrusted to authorities in specific fields, and the extensive bibliographical references at the end of each chapter are indicative of how well the jobs were done. The subjects reviewed for the year of 1942 and their reviewers follow: Historical and Statistical Review (T. R. Dawson); Planting and Production of Raw Rubber and Latex, Gutta-Percha, Balata, Chicle and Jelutong (T. R. Dawson); Properties, Applications and Utilization of Latex (C. F. Flint); Chemistry and Physics of Raw Rubber and Rubber Derivatives, Gutta-Percha, Chicle, Balata and Jelutong (W. J. S. Naunton); Synthetic Rubber (B. J. Habgood); Testing Equipment and Specifications other than for Latex (W. J. S. Naunton); Compounding Ingredients, Accelerators, Antioxidants and Softeners (F. H. Cotton); Fibres and Textiles (W. Knight); Chemical and Physical Properties of Vulcanized Rubber (A. E. T. Neale); Tires (G. A. Shires); Belting (G. F. Payne); Hose and Rubber Tubing (J. Kirkwood); Cables and Electrical Insulation (H. A. Daynes); Footwear (R. C. Davies); Mechanical Rubber Goods (C. H. Birkitt and R. W. Parris); Rubber Flooring (J. Kirkwood); Surgical Goods (C. R. Pinnell); Textile-Rubber Composites, Solvents and Cements (W. N. Lister); Sponge Rubber (W. D. Guppy); Hard Rubber (B. L. Davies); Works Processes and Materials, Including the Treatment of Raw Rubber in the Factory and the Treatment of Vulcanized Rubber (F. H. Cotton); Machinery and Appliances (E. Morris). The author and subject indexes are as carefully compiled and cross-referenced as in previous editions. [From *The Rubber Age* of New York.]

NATURAL RUBBER AND SYNTHETIC RUBBER. Norman Bekkedahl. Instituto Agronômico do Norte, Belem, Para, Brazil. 16 pages.—This pamphlet presents both in English and Portuguese a paper presented by Dr. Bekkedahl, of the National Bureau of Standards, Washington, D. C., as given at the Instituto Agronômico do Norte in Belem on November 5, 1943. The author is on leave from the Bureau of Standards to serve as chief of the rubber laboratory of the Institute at Belem. The history of the analysis and synthesis of rubber is described, including a discussion of Buna-S and Buna-N, and the physical properties of the synthetics compared with those of natural rubber, with special reference to use in tires. Other uses of rubber in war and peace are mentioned, and the paper concludes with the suggestion that Brazil should not neglect her vast possibilities in the rubber program, particularly in the fields of botanical and chemical research aimed at the production of improved natural rubbers. [From the *India Rubber World.*]

ENCYCLOPEDIA OF SUBSTITUTES AND SYNTHETICS. Edited by Morris D. Schoengold. Published by the Philosophical Library, 15 E. 40th St., New York, N. Y. 1943. Cloth, 9¼ by 6 inches, 382 pages. Price $10.00.—Some of the themical and physical properties of a large number of raw materials, chemicals, and products offered recently as substitutes for things difficult to obtain by many branches of industry are described, sometimes adequately, sometimes not, in this encyclopedic volume. The author had the assistance of about 75 manufacturers and four government agencies in securing the material for the compilation. Of interest to the rubber industry is the listing of a variety of replacements that may be used instead of materials formerly employed as bleaching, dehydrating, and emulsifying agents; catalysts; coatings, gums, and impregnants; compounding ingredients; plasticizers; and resins. All the well-known synthetic rubbers and many of the less used ones and a number of rubber substitutes are included. But often the information is of a general rather than specific nature. Two examples will suffice: "Guayule: a shrub native to Mexico with a high proportion of rubber"; and Buna-S "is said to resemble natural rubber to some extent". Cross-references are inadequate, and the encyclopedia as a whole appears to be a hastily compiled catch-all of chemical knowledge, lacking sufficient and precise detail as well as the integration demanded by a volume of this type. There is an index of 264 trades names, and a subject index which is not exhaustive in content. [From the *India Rubber World*.]

ABSTRACTS ON SYNTHETIC RUBBER (IN TWO PARTS): PART I—ARTICLES; PART II—PATENTS. By Muriel E. Whalley. Issued by National Research Council of Canada, Ottawa, Canada. 8½ x 11 in. each. Part I, 362 pp. Part II, 200 pp. Mimeographed. Price: $2.00 for each Part.—This publication, arranged in two parts for convenience of reference, contains a selection of abstracts dealing with processes of manufacture of the various synthetic rubbers and related subjects and the properties which have been recorded for the unvulcanized and, to a lesser extent, the vulcanized material. Abstracts covering uses have also been included, but in this case the selection has been based chiefly on the characteristic properties of each particular type of synthetic rubber. Part I consists of 829 abstracts of articles, arranged in alphabetical order by authors, with a selected subject index and a bibliography of 123 articles and books. Part II comprises 714 abstracts of patents arranged in chronological order, with an index of patentees and a numerical patent index arranged according to countries. The compilations were made from existing bibliographical sources, including *Chemical Abstracts*, *Summary of the Current Literature*, and the Marchionna and Cable bibliographies. [From *The Rubber Age* of New York.]

MODERN SYNTHETIC RUBBERS. (2ND EDITION). By Harry Barron. Published in England. Distributed by D. Van Nostrand Co., Inc., 250 Fourth Ave., New York, N. Y. 6 x 9 in. 355 pp. $6.50.—Whenever there is a need for anything, someone invariably supplies it. There has been such a need for a book on synthetic rubber, and Dr. Barron has filled it admirably. This second edition of his book is packed full of excellent information on this pertinent and topical subject. It is written in a clear and understandable style, and the text is enhanced by the inclusion of many excellent charts, structural organic formulas, and 167 tables. Charts and tables take the place of thousands of otherwise needed additional words in the text. [EDITOR'S NOTE:

Although termed the "second edition", this edition is the first available for general distribution in this country. The original edition had a limited printing, and distribution with few exceptions was confined to England.] In the preface the author tells of his enthusiasm for synthetic rubber and bemoans the fact that so little research on it has been carried out in his own country—Great Britain. "We have certainly been traveling on the train of progress", he writes, "but with our backs to the engine—and third class"! Then he discusses the work in the United States and states frankly and very nicely: "The difficulties of handling the new materials have been tackled with commendable thoroughness. Moreover, what is perhaps more laudable, the results have been published". Later he states: "It is a fact that nearly all the great technical developments associated with rubber have emerged from the consumers and not from the growers. Rubber owes its eminence and importance almost entirely to the efforts of the tire manufacturer (notably in the U.S.A.), whose technical developments have been amazing." The book is up-to-date, is well printed on good quality paper, and contains about 24 photographs on special coated stock. In the text there are many quotations from the literature to substantiate the author's statements, and at the end of each chapter, there is a list of pertinent references to articles and books. There are many outlines of practical methods of preparing substances, conducting polymerizations and making rubber compounds. There are also excellent name and subject indices, which cover seventeen pages alone. Typographical errors are few and generally obvious. There are a few inconsistencies in dates, such as: pages 293 and 295 (Semon began his work at Goodrich in 1926, not 1925); pages 163 and 222 (Neoprene appeared on the market in 1932, not 1930); page 272 (Thiokol has been available commercially since 1930, rather than 1931 as stated). On page 320 it is stated that "no method exists for the direct estimation of natural rubber in a compound." Since the writing of this book a method for this purpose has been developed using the infrared spectrograph (Barnes, Liddle & Williams, *Ind. Eng. Chem. Anal. Ed.*, Vol. 15, No. 2, pages 83–90, February 15, 1943; reprinted in *Rubber Chem. & Tech.*, Vol. 16, No. 3, pages 634–649, July, 1943). The contents of the book are divided into three major parts. To show the scope of the book, a list of these parts and their subtopics is given: Part I—General Considerations: natural rubber and synthetic rubberlike materials; economics of synthetic elastic materials. Part II —Chemical and Physical Background of Synthetic Elastic Materials: terminology; historical background of synthetic elastics; chemical behavior and structure of natural rubber; raw materials; polymerization and copolymerization. Part III—Technology of Synthetic Elastic Materials: elastomers—S.K.B., Buna rubber, Perbunan, Hycar, Chemigum, Neoprene, polyisobutylene, Butyl rubber; Thiokol; ethenoid plastics (vinyl products, Koroseal, Butacite, acrylic derivatives); ethyl cellulose; and additional comparative properties of elastics. [From *The Rubber Age* of New York.]

THE OUTLOOK FOR SYNTHETIC RUBBER. By Melvin A. Brenner. Published by National Planning Association, 800—21st St., N.W., Washington 6, D. C. 5¼ x 7½ in. 36 pp. 25c per copy (lower price in quantity).—Although there has been much comment on the postwar status of both synthetic and natural rubber, this pamphlet is the first public report which has drawn together all existing information on both sides of the question. And, we might add, it represents a good job. Specifically, the report, one of a series of "planned pamphlets" prepared for general distribution on economic angles by

the National Planning Association, a privately financed, nonprofit, nonpolitical organization, discusses the development of the synthetic rubber industry since its inception about ten years before Pearl Harbor and its tremendous growth until the present time. It covers the nature of synthetic rubber, the history of the industry, its present program, and its postwar survival prospects. The author, Melvin A. Brenner, is an economic analyst with the War Production Board, and the report is adapted from a study made by him when he was associated with the National Resources Planning Board. It is Mr. Brenner's premise that the postwar status of synthetic rubber will depend on three things: (1) world rubber supply and demand; (2) the competitive position of synthetic rubber to meet postwar markets; and (3) Government policy. He treats with each of these factors briefly, but thoroughly. The report includes charts and tables, several taken from various progress reports issued by the Rubber Director, and covers five broad heads, as follows: Synthetic Rubber before Pearl Harbor; Synthetic Rubber Since Pearl Harbor; Postwar Rubber Supply and Demand; Competition Between Natural and Synthetic Rubber; and Government Policy and Outlook for Present Facilities. Every rubber manufacturer should secure a copy of this pamphlet for reading by both his technical and sales forces. [From *The Rubber Age* of New York.]

CHEMICAL NAMES AND TERMS FREQUENTLY ENCOUNTERED IN THE SYNTHETIC RUBBER INDUSTRY. Hycar Chemical Co., Akron, O. 8 pages.—A glossary of the more important words in the field of synthetic rubber and rubber-like plastic materials recently prepared by the Hycar Chemical Company is presented in this booklet as a guide to proper pronunciations and meanings, and as a service to business and industry. It is stated that the glossary is by no means complete, but does include the more common chemical terms and some of the well-established trade names. The booklet should be of considerable help in clearing up some of the confusion concerning these new terms that is evident in many places. [From the *India Rubber World.*]

SYNTHETIC RESINS AND RUBBERS. By Paul O. Powers. Published by John Wiley & Sons, Inc., 440 Fourth Ave., New York, N. Y. 5½ x 8½ in. 296 pp. $3.00.—This is the first single volume to cover the chemistry of synthetic resins and rubbers. Specifically, the book describes briefly the chemistry of polymers, particularly those of commercial importance, and their applications. A good deal of the material used is similar to that used in ESMDT and ESMWT courses in plastics given at Franklin and Marshall College by the author and others. The author, incidentally, is Chief of Organic Research of the Armstrong Cork Company. The book is divided into six parts, as follows: (1) Theories of polymer formation; (2) Condensation polymers; (3) Vinyl polymers; (4) Synthetic rubbers; (5) Resins from natural products; and (6) Application of synthetic resins. In addition to a number of references furnished at the end of each section, there is also a series of review questions. These questions enable the student to improve his self-education. The section on synthetic rubber, written by K. H. Weber, of the Armstrong Cork Company, is very well done. Starting with the chemistry and structure of natural rubber, Dr. Weber then covers polychloroprene, polybutadiene, polysulfide and polybutene rubbers. Polymerization, structure, manufacture, properties and application are discussed for each type of synthetic and some theories reviewed. An interesting historical outline of synthetic polymer developments is included in the book, which also has a carefully cross-referenced subject index. [From *The Rubber Age* of New York.]

1944 YEARBOOK. Los Angeles Rubber Group, Inc., Mayfair Hotel, Los Angeles, Calif. 8½ x 11 in. 24 pp.—Dedicated to "the chemists and compounders who are shouldering a full share of the conversion from natural to synthetic rubbers", the latest edition of the *Yearbook* issued by the Los Angeles Rubber Group is the largest published to date. Like previous editions, it includes a list of officers, committee members and the group's full membership, in addition to lists of rubber manufacturers and suppliers on the Pacific Coast, the latter taken largely from the current edition of the "Rubber Red Book". Also included is a list of synthetic rubbers, identified by chemical designation and supplier, as well as a list of the plants producing GR-S, and their operators, in the Rubber Reserve program. The carbon black nomenclature recently approved by the Office of the Rubber Director is shown. Finally, the current edition reviews the group's activities, meeting by meeting, in 1943; contains a full page description of last summer's outing at the Uplifters Club in Santa Monica; and reproduces the latest by-laws. Advertising was accepted for the first time. [From *The Rubber Age* of New York.]

PRODUCING FOR WAR—PREPARING FOR PEACE. Firestone Tire & Rubber Co., Akron Ohio. 8½ x 10½ in. 36 pp.—What Firestone is doing to help win the war and what some of its plans are for the production of civilian goods when peace has been declared are outlined in this new booklet. Some of the myriad products produced by the company for the Armed Forces, including life rafts, vests, tires, gliders, gas masks, tank gun turrets, trench mortar bases, spark plugs, helmets, fuel cells, pilot seats, high-altitude oxygen tanks, and airplane parts, are illustrated. Postwar plans call for the manufacture and distribution of Velon, Contro, Foamex, metal alloy and rubber-to-metal products. The book is attractively printed. [From *The Rubber Age* of New York.]

THE STORY OF SCRAP RUBBER. Howard Wolf. Published by A. Schulman, Inc., Akron, O. 1943. Cloth, 9¼ by 6 inches, 112 pages. Illustrated.—The coauthor of that absorbing volume, "Rubber: A Story of Glory and Greed", has written a concise history of the scrap and reclaim industries, pictorially enhanced with more than a score of large photographs which show all the important operations of salvaging used rubber. Rubber business, Wolf points out, began as a scrap industry in the late Eighteenth Century, when Portuguese sea captains, the first rubber dealers, offered articles made by South American Indians which could be used to remanufacture various rubber articles desired in this country and in Europe. An account is given of the various reclaim invention developments which preceded the perfection of the alkali digestion reclaim process in 1899 by Arthur Hudson Marks. He it was who made the scrap rubber industry possible. Its rapid growth in the Twentieth Century is one of the most interesting sagas of American enterprise, which has the impact of a dramatic climax in the war years when scrap saved the rubber situation of the United Nations in the interval of waiting for the required synthetic production. The final chapter stresses the achievements and unsolved problems in reclaiming synthetic scrap rubber. The specifications for scrap rubber of the Rubber Reclaimers Association, Inc., as revised November 7, 1941, are given in an appendix. The volume is sponsored by A. Schulman, Inc., scrap rubber suppliers for the reclaim industry. [From the *India Rubber World*.]

THE RUBBER INDUSTRY AND THE WAR. General Bulletin No. 1961. The Rubber Manufacturers Association, Inc., 444 Madison Ave., New York, N. Y. 80 pages.—This attractive pictorial presentation summarizes the war story of

some 500 American rubber manufacturers. Briefly, concisely, by word and picture, is revealed rubber's contribution to the war effort, including tires, bogie wheels, fuel cells and tanks, rafts, bridges, barrage balloons, gas masks, footwear, rubberized fabrics, mechanicals, and druggists' sundries. Also covered are nonrubber products, such as planes, munitions, and chemicals. Sections on synthetic rubber and rubber conservation conclude this interesting booklet designed to show the general public how the rubber industry is doing its part to help win the war. [From the *India Rubber World.*]

THE STORY OF THE RUBBER LIFE RAFT. By Edgar G. Wandless. Privately printed by the New York Rubber Corporation, 9 Rockefeller Plaza, New York 20, N. Y. 5 x 7 in. 48 pp.—Here is a story that needed writing—the history and development of the rubber life raft which is saving so many valuable lives in the current global conflict. The story is told in detail from the pioneering days—which go back only to the 1910's—up to and including the modern devices which are provided with miscellaneous equipment not only to keep the occupant afloat, but fairly well-fed and healthy. The book, attractively printed and containing several interesting illustrations, is divided into six chapters, as follows: (1) Introduction; (2) The Pioneering Days; (3) Men and Rafts Against the Sea; (4) The Raft; (5) The Equipment of the Raft; (6) When the Raft Comes Home from the War. The role played by the New York Rubber Corporation in supplying these vital craft for the war effort is threaded into the story itself. [From *The Rubber Age* of New York.]

PHYSICAL CONSTANTS OF THE PRINCIPAL HYDROCARBONS. Fourth Edition. M. P. Doss. Published by the Texas Co., New York, N. Y., at the request of the Petroleum Industry War Council. Cloth, 11 by 8½ inches. 215 pages. $3.75.—This book, prepared mainly for laboratory workers, lists in one volume the most recent and authoritative physical constants on more than 2,000 hydrocarbons, many of which are related to the manufacture of aviation gasoline, synthetic rubber, synthetic resins, etc. Although the tabulation does not claim to be complete, it is believed to include data on most of the aliphatic hydrocarbons so far isolated or synthesized, and this is also stated to hold true to a lesser degree for the cycloparaffins (naphthenes) and such unsaturated ring hydrocarbons as the cycloolefins, etc., as well as the mononuclear aromatics. Only the principal members of the polycyclic series are given, mainly those that have actually been isolated from petroleum residues, etc., such as picene, pyrene and anthracene. As stated in the introduction, where there is a disagreement in the literature with regard to certain values, the most recent data have been used. In some cases calculated values have been employed, particularly for heats of vaporization and combustion, but in all cases the data given are accompanied by the literature references so that in case of doubt as to the accuracy of the value given, the original work may be consulted with regard to the purity of the hydrocarbon investigated, method or formula employed for determining the constant, or other pertinent information. The book includes space devoted to an explanation of nomenclature used and units used in the tables and an index of the hydrocarbons covered. [From the *India Rubber World.*]

TECHNICAL DATA ON PLASTIC MATERIALS. Prepared by Plastics Materials Manufacturers Association, Tower Building, Washington, D. C. 8½ x 11 in. 141 pp. $1.50.—The nature, particular merits and utility of various plastic

materials, with their property values as measured by recognized methods, are outlined in this manual, prepared by the P.M.M.A. as a service to the representatives of governmental agencies concerned with the use of plastics materials in the war effort. Brief, explanatory forewords are followed by tables and charts of more detailed data. For simplification, individual materials very similar in composition and properties have been considered as members of groups or types for which data is given. Materials for which data is given include casein plastic, ethyl celluloses, phenol-formaldehyde moulding materials, polystyrenes, vinylidene chloride, and vinyl chloride-acetate resin compounds. A list of member companies is also included. [From *The Rubber Age* of New York.]

PLASTICS CATALOG: 1944. Published by Plastics Catalogue Corp., 122 East 42nd St., New York 17, N. Y. 8½ x 11½ in. 990 pp. $6.00.—The history and achievements of plastics materials in every branch of industry are brought up-to-date in this latest edition of the "encyclopedia of plastics". In addition to listing data on plant and personnel of the industry, the current edition is replete with information of special importance, including 40 selected war case histories representing typical plastics developments used by the various branches of the Armed Forces. Other sections are devoted to tests and specifications, materials, engineering and molding, fabricating and finishing, machinery and equipment, laminates, coatings, synthetic fibers and finally, synthetic rubber and rubberlike plastics. This latter section has been expanded to 40 pages, and furnishes data on the butadiene, chloroprene and isobutene-diolefin polymers and copolymers, as well as on organic polysulfides, isobutene and vinyl polymers, elastomeric styrene derivatives, polyester elastomers, vulcanizable vegetable oil polymers, and cyclorubbers. Included also is a chart outlining the properties of the various synthetic rubbers and rubberlike materials. The contents of this latest plastics catalog are truly encyclopedic in scope. [From *The Rubber Age* of New York.]

A.S.T.M. STANDARDS ON PLASTICS. Published by the American Society for Testing Materials, 260 S. Broad St., Philadelphia 2, Pa. October, 1943. Paper, 9¼ by 6 inches, 431 pages. Price $2.00.—The 85 specifications, tests and definitions in the latest compilation of standards on plastics indicate the extensive work done in this field by the American Society for Testing Materials. In 1943 more than 25 new specifications and tests were standardized, with particular emphasis on purchase specifications. There are four standards on nonrigid plastics and 18 specifications covering numerous types of moulding compounds and other plastics in the form of sheets, tubes, and rods. There are methods of tests covering distortion, hardness, tear resistance, thermal expansion, stiffness, tensile properties, compressive strength, dielectric constant, flammability, color-fastness to light, diffusion of light, and mar resistance. Tests methods are included for the compression set of vulcanized rubber, low-temperature brittleness of rubber and rubberlike materials, compressive strength of electric insulating materials, hardness of rubber, durometer indentation, hardness of rubber, tear resistance of vulcanized rubber, and tension of rubber, which were prepared under the jurisdiction of Committee D-11 on Rubber Products and D-9 on Electrical Insulating Materials. A tentative standard for descriptive nomenclature of objects made from plastics, and a standard of terms relating to the rheological properties of matter also are included. [From the *India Rubber World.*]

A.S.T.M. Standards on Textile Materials (with Related Information). American Society for Testing Materials, 260 S. Broad St., Philadelphia 2, Pa. October, 1943. Paper, 9¼ by 6 inches, 458 pages. Price $2.25.—Methods of testing, specifications of textiles and related materials, and definitions and terms developed by Committee D-13 of the Society and considerable other data and related information useful to those who deal with textile materials are included. In the cotton section are specifications and methods for holland cloth, tire fabrics, other than cord fabrics, hose and belting fabrics, goods for rubber and pyroxylin coating; specifications for 0.007-inch cotton tape for electrical purposes; methods and tolerances for tire cord, woven and on cones, and carded gray goods; and specifications for tolerances of numbered duck. Methods for tolerances for rayon tire cord, woven and on cones, are among 11 requirements for silk and rayon. Six standards pertain to asbestos tape. Several general standards on such subjects as air permeability, fire-retardant properties, color fastness to light, finishes, and resistance to insect pests, micro-organisms, and water are included in the first section of the book. There are also an extensive glossary of textile terms, a list of man-made and natural fibers, a table of terms relating to hand of fabrics, and a series of definitions and photographs of defects in woven fabrics. [From the *India Rubber World*.]

Standards on Electrical Insulating Materials (with Related Information). Prepared by Committee D-9. Published by the American Society for Testing Materials, 260 So. Broad St., Philadelphia 2, Penna. 6 x 9 in. 515 pp. $2.75.—This publication gives in their latest form the more than 75 A.S.T.M. standards, specifications and methods covering electrical insulating materials and related products. In addition to the 56 specifications developed by the Society's Committee D-9, there are 18 other standards to make the book complete pertaining to certain plastics, rubber, textiles, paper products, etc. New material included gives requirements for phenolic moulding compounds; laminated thermosetting materials; vulcanized fibre sheets, rods, and tubes; measuring dimensions of rigid rods; natural block mica and mica films suitable for use in fixed mica-dielectric capacitors; orange shellac and other lacs; low and medium-voltage pin-type lime glass insulators; and tensile properties of plastics. Most of these items were developed and published first in 1943. There are 8 standards covering various types of insulating varnishes, paints, lacquers, and their products. Sixty-five pages are devoted to the fifteen methods and specifications for moulded insulating materials. A section on plates, sheets, tubes and rods includes 13 widely used standards. There are 3 standards on mineral oils and 5 relating to ceramic products (glass, porcelain, steatite). The 7 standards covering various electrical tests comprise 70 pages. There are sections covering insulating paper, mica and rubber products, textile materials, conditioning, enclosures, and servicing units. An interesting part of the publication is the section giving references on significance of tests of various electrical insulating materials. [From *The Rubber Age* of New York.]

Emulsion Technology. Published by Chemical Publishing Co., Inc., 26 Court St., Brooklyn, N. Y. 5½ x 8½ in. 290 pp. $5.00.—The symposium on emulsions held by the British Section of the International Society of Leather Trades' Chemists some time ago, brought together some of the foremost European colloid chemists. The papers presented at that symposium were originally published under the title of "Technical Aspects of Emulsions", which ran to three editions and which is now out of print. Because of the numerous re-

quests for that book and because of new developments in emulsion technology, it was decided to bring out a new edition with certain revisions and additions—the latter by American specialists. This book is the revised edition. To round out the theoretical and practical aspects of emulsion in the original book, there have now been added a section by M. P. Hoffman, an authority on the use of colloid mills and homogenizers; a section by R. M. K. Cobb, an authority on paper treating emulsions; and a section by S. Werthan, a specialist on water—emulsion paints and other coatings. Authoritative data on methods and formulation of many practical commercial emulsions in the drug, cosmetic, beverage, wax, coating and paint fields has also been added, as well as a comprehensive list of all important commercial emulsifying agents. The current edition has 15 chapters in all, including one on latex by H. P. and W. H. Stevens, of England, and a cross-referenced subject index. Like the first edition, it serves to bridge the gap between theory and practice. [From *The Rubber Age* of New York.]

HANDBOOK OF CHEMISTRY (FIFTH EDITION). Compiled and Edited by Norbert Adolph Lange. Published by Handbook Publishers, Inc., Sandusky, Ohio. 5⅜ x 7¾ in. 2092 pp. $6.00.—The latest edition of this reference work of chemical and physical data used in both laboratory and factory has been completely revised and brought up to date. All of the subject matter in the previous edition has been retained, with one or two minor exceptions, in addition to which a number of new tables appear. These include a periodic table (Deming) and tables on flammable liquids, flame temperatures, plastics, fluorescence of chemicals, minerals and gems, and water for industrial use. Many of the previously included tables have been extended or completely rewritten, including those on the physical constants of organic compounds, nomenclature of organic compounds, trade names of chemicals, and organic reagents for inorganic analysis. This new edition is supplied with an unusually complete index, covering more than 3,600 entries, occupying 28 pages, two columns to the page. An advantage to the user is the fact that it makes use of a large size page, good quality non-glare paper, with a size and style of type that makes reading easy and accurate. The section on synthetic rubber, which could easily be expanded in the light of more recent information, is taken from the circular letter prepared by L. A. Wood for distribution by the National Bureau of Standards in 1940. [From *The Rubber Age* of New York.]

PHYSICAL METHODS OF ANALYSIS OF SYNTHETIC AND NATURAL RUBBER *

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Reports have been made that more than three thousand kinds of rubberlike synthetics have already been prepared. Obviously, not all are of practical importance, nor can they legitimately be referred to as "synthetic rubbers", but a certain select group of these, as well as still other new synthetics, will survive and prove meritorious. Uses will be found for these new synthetic rubbers, both alone and when blended with other synthetics or with natural rubber. The rubber chemists of the future will, therefore, be faced with the problem of analyzing such mixtures. Because the components of these mixtures are often complex and their degradation products are not well known, it will be difficult, by conventional analytical methods, to establish their identities or the proportions in which they are present.

In anticipation of these difficulties, it was deemed advisable to study the applicability of various physical tools to this and other problems of the rubber industry. In a previous publication[1] the authors called attention to the fact that infrared spectroscopy could be of value in differentiating between rubbers and in analyzing rubber mixtures, and pointed out that the infrared absorption spectra of the various rubbers are unique and offer one means of attacking the analytical problem outlined. However, in this preliminary paper the analytical possibilities were merely noted without any attempt to reduce them to practice.

Shortly after the completion of this preliminary study, the authors were called by the War Production Board to analyze a series of captured German tires and inner tubes for the Army Ordnance Department, and to determine, if possible, the amounts and types of synthetic rubbers which had been blended with natural rubber in the manufacture of these tires. As a result of this investigation, two satisfactory methods of analysis were developed.

The first, the determination of the phosphorus content, furnishes a simple method for measuring the relative amounts of natural and synthetic rubbers present in an unknown; the second, the application of infrared spectroscopy, makes it possible to determine both the type of each rubber and the amounts present. In conjunction with the latter analysis, a method was devised for separating from compounded rubber products a sample of rubber hydrocarbon free of pigment and filler. The details of the preparation and analysis of samples are given, together with a typical set of data obtained in connection with the tire and tube studies.

Although these methods may not necessarily be successful in solving every type of rubber mixture analysis encountered, their value in this particular problem warrants careful consideration in connection with similar problems which may arise in the future.

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DETERMINATION OF RATIO OF NATURAL TO SYNTHETIC RUBBER BY PHOSPHORUS CONTENT

The metabolic processes of plants birng about, within the various parts of the plant, the deposition of a great many of the metals commonly found in the soil. In contrast with this, the metals found in any synthetic product are limited to those purposely added and those accidentally introduced by contact with the pieces of processing equipment.

To determine whether this difference might prove to be valuable for analytical purposes, samples of natural and synthetic rubbers were subjected to an ultraviolet spectrochemical analysis, using a large Hilger E-1 spectrograph. Table I shows the results of such a comparative emission analysis. It may

TABLE I

ULTRAVIOLET SPECTROCHEMICAL ANALYSIS OF THE METAL CONTENT OF RUBBER HYDROCARBONS

	Natural rubber					Synthetic rubber		
	Smoked sheet	Crepe rubber	Tread stock	Carcass stock	Reclaimed tires	Domestic Buna-S	German Buna-S	Buna-S tread stock
	Per cent ash							
	(0.27)	(0.17)	(3.6)	(32.5)	(23.2)	(1.49)	(2.11)	(6.3)
Aluminum	2−	2−	2+	2−	3−	2−	2+	2
Antimony	0	1	0	0	2	0	0	0
Barium	1+	1+	1+	1+	3−	2−	2−	1+
Boron	1+	1+	2−	2−	1	1+	1+	2−
Cadmium	0	0	1	1+	2−	0	1−	1
Calcium	2	2	2+	2−	3−	2+	2+	3−
Chromium	1	1	1+	0	2−	1+	1+	2−
Copper	2−	2−	1+	1+	2−	2−	2−	1+
Iron	2−	2−	2	2	2	2	2	2
Lead	1	1	1+	2−	2	1+	1+	1+
Magnesium	2+	2+	3−	2+	3−	2+	3−	3−
Manganese	1	1	1+	1	1+	2−	1+	1
Molybdenum	0	0	0	0	2−	0	0	0
Nickel	1	1	1+	0	1+	1+	1+	2−
Phosphorus	2+	2	2+	2	2	0	1+	0
Potassium	2	2	0	0	2−	2−	0	1+
Silicon	2	2	2+	2	2+	2	2+	3−
Sodium	2	2	2	2	3−	2+	2	2+
Strontium	1+	1+	1	0	2	1+	1+	1
Tin	1	1	1	1	1	1+	1	1
Titanium	1+	1	1+	1	2	1	2	1
Vanadium	0	0	0	0	0	0	2−	0
Zinc	2−	2−	3−	3	2+	2	2−	3−

Ranges for qualitative estimates:

3 = 100 to 1.0%
3− = 10 to 0.10%
2+ = 1.0 to 0.01%
2 = 0.1 to 0.001%
2− = 100 to 1.0 p.p.m.
1+ = 10 to 0.10 p.p.m.
1 = 1.0 to 0.01 p.p.m.
1− = less than 0.1 p.p.m.
0 = metal not detected

be seen at once that, whereas the synthetics contain little or no phosphorus, this element is present in the natural rubbers in readily detectable quantities. This clue was followed up in great detail, and the exact values for the phosphorus contents were determined through the use of another spectrochemical tool, the visible light spectrophotometer. The details of the exact procedure followed are given below.

Table II gives the phosphorus contents of a variety of natural and synthetic rubbers. These values show a considerable variation for natural rubbers of different origins, but all may be characterized by high phosphorus (average 400 p.p.m). when compared with typical synthetics (average 20 p.p.m.). Thus, an exact phosphorus determination should make possible a determination of the ratio of natural to synthetic rubber in an unknown sample.

Figure 1 was plotted to show that the phosphorus could be determined accurately enough to allow the content of this element to be used as a yardstick and as a direct measure of the amount of natural rubber present. (If the origin of the natural rubber is unknown, the slope of this curve is not determinable, and the method is only roughly quantitative. On the other hand,

TABLE II

PHOSPHORUS CONTENT OF VARIOUS RUBBERS

	P.p.m.		P.p.m.
Natural rubber		Synthetic rubber	
Smoked sheet A	690	Buna-S (American)	15
Smoked sheet B	380	Buna-A (German)	30
Smoked sheet C	320	Cotton tire cord	210
Smoked sheet D	500	Viscose tire cord	10
Smoked sheet E	400		
Crepe	490		
Pale crepe	350		
Reclaimed tube	390		
Guayule	200		

if a sample of the natural rubber used in compounding is available for a phosphorus test, a much higher degree of accuracy may be expected.) In spite of the variation of the phosphorus content of natural rubbers of different origin, a reasonable first guess at a mixture of unknown constitution may be based on the following generalization:

High phosphorus (300 to 450 p.p.m.)	= natural
Medium phosphorus (100 to 250 p.p.m.)	= natural + synthetic
Low phosphorus (0 to 50 p.p.m.)	= all synthetic

As will be seen from Table IV, the above method provides a very simple approximate analysis. The agreement between this and the more exact infrared method is indeed surprising. However, the method is always open to the uncertainty that phosphorus may have been introduced in processing and not been eliminated in the sampling procedure.

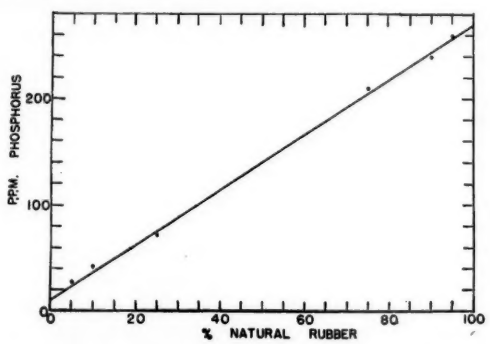


FIG. 1.—Phosphorus in carcass stock compounded with natural rubber and Buna-S.

Formula of stock	
Rubber hydrocarbon	100
Zinc oxide	50
Stearic acid	1
Pine tar	1.5
Agerite Resin	1.5
Sulfur	2.0
Altax	1.25

Although any sensitive method for determining the phosphorus will be satisfactory, the spectrochemical procedure detailed below was found to be most suitable. This colorimetric method is based on many literature references of which Zinzadze[2] and Goodloe[3] are typical. An intense blue color is produced in solutions containing phosphorus by reduction of phosphomolybdate, the intensity of the color being directly proportional to the phosphorus content of the solutions. In this laboratory, the color values or percentage transmissions were measured on a General Electric recording spectrophotometer. The blue color which develops has a rather broad spectral width, which can be measured satisfactorily by means of any ordinary comparison colorimeter, although the increased precision of the more accurate photoelectric instruments is to be preferred. Figure 2 shows a series of transmission curves for standard phosphorus solutions.

Preparation of Sample.—All glassware and reagents must be free of phosphorus, and a suitable blank or control must be carried through the complete procedure.

Other possible sources of extraneous phosphorus are the cord and plasticizer used in fabrication. [It is interesting in this connection to note (Table II) that cotton, or natural fibers are high in phosphorus, whereas synthetic fibers, rayons, etc., have a low content, thus enabling a distinction to be made between these two types of fibers. Undoubtedly other cases of natural *versus* synthetic materials may arise in which this general method might be of help.] Therefore, it is advisable that all cords, if present, be removed by the following procedure: A section of the rubber (tire) is shredded in a two-roll mill, then mixed with water in a Waring Blendor. After 5 to 10 minutes' stirring, the cord can be partially separated by decantation. The remaining cord is digested at about 4° C for 18 hours with an excess of cuprammonium solution [see Clibbens and Gaeke[4] and the committee of the American Chemical Society[5] for preparation of this solution]. The material is washed free of cuprammonium with water and then dried. If the sample is a prepared rubber stock, all phosphate-containing plasticizers must be removed by refluxing the shredded rubber for 8 hours in a Soxhlet extractor with a solvent composed of 68% chloroform and 32% acetone.

For maximum photometric accuracy, a weight of rubber should be taken such that a phosphorus content up to 0.080 mg. is contained. With synthetic rubbers, a 1-gram sample is suitable, whereas, with natural rubber, approximately 0.1 gram is used. To ensure a representative sample, a larger weight is taken and subjected to the preliminary preparation. The color value of a 1-gram equivalent is then measured to furnish a rough idea of the phosphorus content. With this as a basis, a weight of sample is chosen according to the above criterion and is measured accurately.

Preferably, the phosphorus values should be calculated to the weight of rubber hydrocarbon, the carbon, zinc oxide fillers, etc., having been removed previously. This was not always done in the authors' work, as the carbon analysis was done elsewhere; hence, the phosphorus content of the samples reported here was based on the entire rubber sample.

Ashing of Sample.—The weighed sample of extracted rubber is ashed in a suitable crucible in a controlled furnace at a temperature not higher than 600° C, until free of organic material. This must be done slowly enough to prevent the material from kindling. It was found unnecessary to add a phosphorus fixative in the case of rubber materials, as no increased phosphorus values were obtained by adding zinc oxide to prevent the volatilization of

phosphorus. After cooling, the residue is dissolved by boiling in just sufficient dilute sulfuric acid to dissolve the soluble materials. Excess acid is to be avoided, since the final acidity is very important, but an excess of acid may be added and later neutralized. A slight turbidity which may be removed by filtering remains in some cases as a result of the presence of a siliceous material. The clear solution of the ashes is transferred to a 50-cc. Pyrex volumetric flask and the volume is adjusted to about 40 cc.

DEVELOPMENT OF COLOR.—Although many procedures are described in the literature, the following modification was used here.

Standard solutions.—Solution I, ammonium molybdate, 5.45 grams [$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$], dissolved by warming with water and made to 100 cc.

Solution II, 10 *N* sulfuric acid (282 cc. of concentrated sulfuric acid diluted to 1000 cc.), checked by titration.

Solution III, stannous chloride.—A stock solution of stannous chloride dehydrate is 40 grams dissolved in concentrated hydrochloric acid (density 1.18) and made up to 100 cc. (stable for months). For use, it is diluted 200 times with distilled water (stable for one day).

Analytical procedure.—To the solution prepared according to instructions above, 2.5 cc. of Solution I and 5 cc. of Solution II are added and mixed thoroughly, and 2 cc. of Solution III are added with constant swirling. The solution is made to volume (50 cc.) and mixed thoroughly. (The final acidity of the 50-cc. sample should be 1 *N* sulfuric acid. If excess acid is used in dissolving the ash, it may be neutralized at that point or the amount of Solution II may be reduced to give the final acidity stipulated.) A blank is carried through the same procedure to check for the presence of phosphorus in the reagents.

DETERMINATION OF PHOSPHORUS CONTENT.—The percentage transmission of the solution in a 1-cm. thick cell at 700 mμ is measured exactly 20 minutes after adding Solution III. The amount of phosphorus in an unknown may be determined from a calibration curve which shows the percentage transmission plotted as ordinates *versus* the phosphorus content of known standard solutions as abscissas. The calibration curve may be prepared from a series of transmission curves such as those of Figure 2.

NOTES ON PHOSPHORUS ANALYSIS.—When a molybdate is added to a solution containing orthophosphate according to the method described above, an insoluble phosphomolybdate is formed. However, because of the high dilution, a precipitate is not apparent. The addition of a reducing agent (stannous chloride) causes a reduction of the phosphomolybdate and gives an intense blue color. Under the proper conditions, the molybdenum reagent necessary as an excess is not reduced.

The factors which affect the color are:

1. The acid concentration is very important. In the presence of too much acid, a light color is produced. Conversely, if too little acid is used, the molybdate reagent itself is reduced, causing dark colors. In the method used, a 20% decrease in acidity results in a 10% increase in color intensity; 10% increase in acidity results in a 10% decrease in color intensity. Soluble silica also produces a blue color with the above reagent if the silica concentration is high or the acidity is insufficient to suppress the ionization of the silicic acid. The acidity chosen as optimum in this investigation (1 *N* sulfuric acid) is such that silica up to 2000 p.p.m. does not interfere.

2. The molybdate concentration is the next most critical factor. An increased molybdate concentration results in a higher sensitivity to phos-

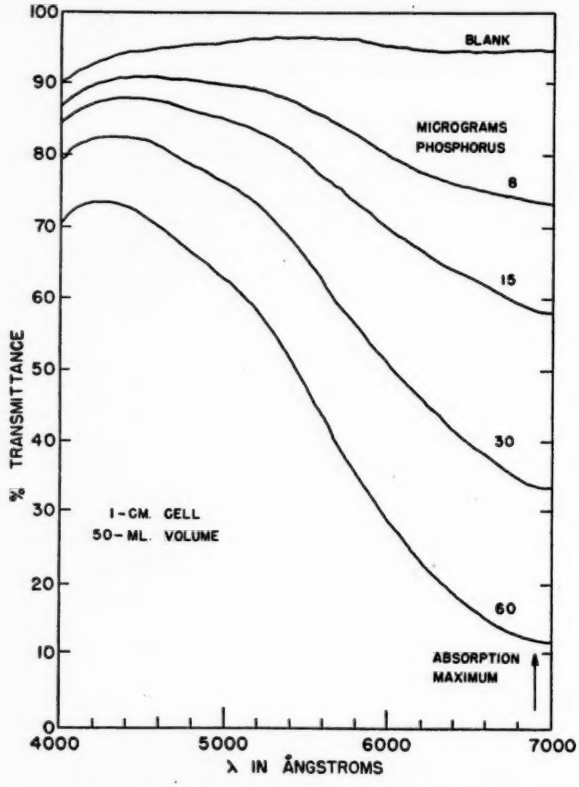


FIG. 2.—Spectrophotometric determination of phosphorus.

Calibration of phosphorus as reduced phosphomolybdate.
Final solution 1 *N* in sulfuric acid, MoO_3 0.13 gram per 50 cc., $SnCl_2 \cdot 2H_2O$ 0.006 gram per 50 cc.

T %	−log *T*	Blank	Net −log *T*	Phosphorus (micrograms)	P, −log *T* (microgram)
94.5	0.024	...	...	None	...
73	0.137	0.024	0.113	8	0.0141
58	0.237	0.024	0.213	15	0.0142
34	0.469	0.024	0.445	30	0.0148
12.5	0.903	0.024	0.879	60	0.0146

phorus, but also an increased blank. A high blank reading is not desirable when low concentrations of phosphorus are present. A 50% increase in the molybdate concentration, as used above, results in approximately a 15% increase in the color intensity. A 20% decrease in molybdate concentration results in approximately a 10% decrease in color intensity.

3. The stannous chloride concentration is not very critical. A ±50% change in the amount of stannous chloride influences the phosphorus result not more than ±5%.

4. Under the given conditions, the color increases for 5 to 10 minutes after the stannous chloride is added and bleaches slowly thereafter. It is recommended, therefore, that the color be measured 20 minutes after addition of the stannous chloride.

5. The following sources of interference have been considered, and methods of reduction or elimination are recommended where necessary:

Ferric ion up to 6 p.p.m. does no harm. Fifteen parts per million slightly inhibit color development, while larger amounts of ferric ion cause very rapid fading of the color. Ferrous ion causes no harm. A Jones reductor with metallic cadmium gives best results for prevention of interference from ferric ion[6].

The presence of more than 20 p.p.m. of titanium causes interference by retarding the rate of color development.

Arsenates give the same color as phosphates, and the intensities are inversely proportional to the molecular weights. Reduction with sodium bisulfite eliminates the influence of arsenates (20 mg. of arsenic pentoxide per 50 cc. may be taken care of by reduction to arsenic trioxide).

Nitrates up to 100 p.p.m. have no effect; 200 p.p.m. reduce the color about 10%.

Sulfates in large amounts interfere, presumably by depressing the ionization of the sulfuric acid.

Tartaric and citric acids interfere above 20 p.p.m., with inhibition of maximum color. They may be removed by oxidation with permanganate.

Aluminum and manganese in reasonable amounts do not interfere.

Calcium and magnesium up to 1000 p.p.m. have no effect.

Nickel up to 1000 times the phosphorus content does not interfere except for its own color.

Trichloroacetic acid begins to interfere with the maximum color development at concentrations above 4% in the final mixture. Acetic acid shows practically no effect.

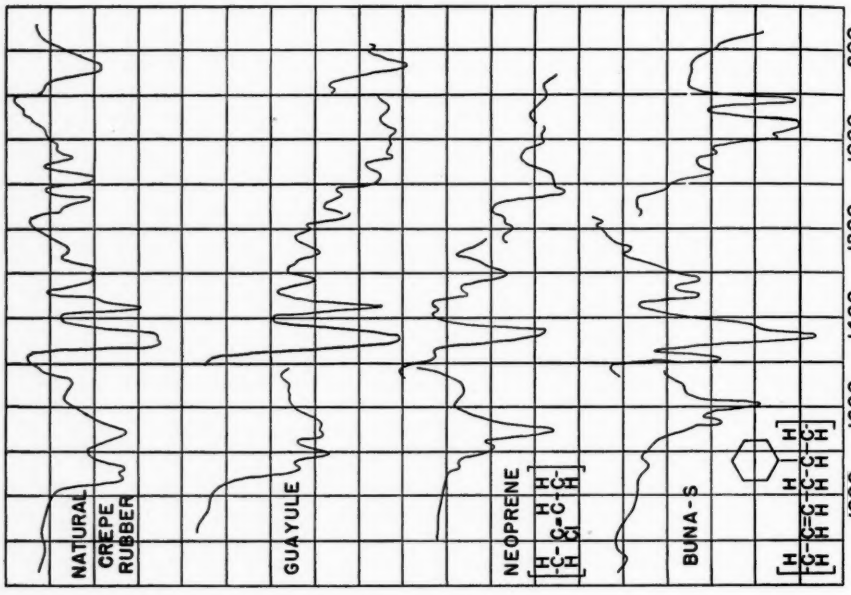
Hydrochloric acid has a tendency to lessen color stability and retards or inhibits maximum coloration.

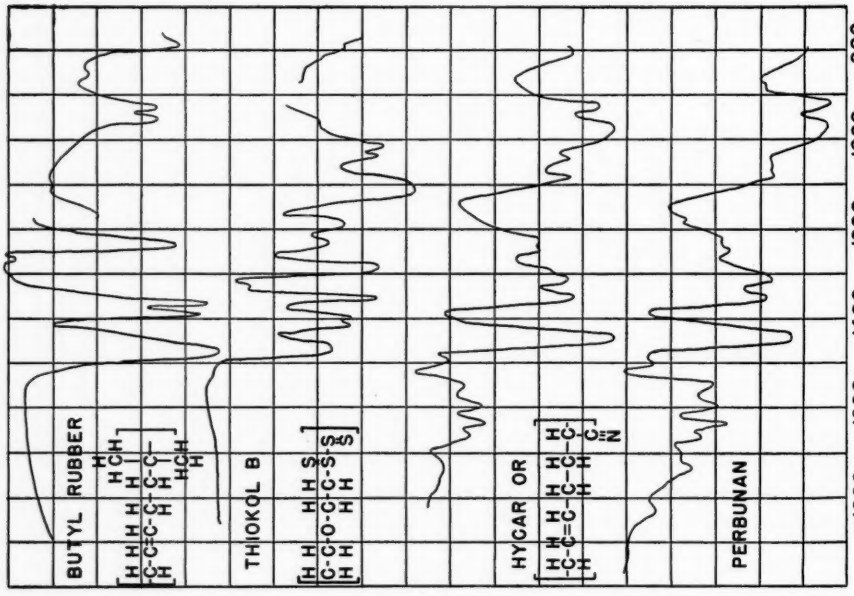
DETERMINATION OF TYPES AND AMOUNTS OF RUBBERS BY INFRARED SPECTROSCOPY

Recent publications[7] have described in great detail the methods and applications of infrared spectroscopy to the identification and analysis of many types of organic materials. It is sufficient here to point out the two salient characteristics of infrared absorption for the basis of analysis to be understood.

In the first place, the infrared absorption spectrum (a plot of percentage transmission as oirdnate *versus* frequency in $cm.^{-1}$) of a material is a unique characteristic of the material and cannot be duplicated by another compound. Some of the absorption bands can be ascribed to particular atomic groups within the molecule; others, characteristic of the molecule as a whole, are particularly useful for such studies as differentiating isomers. Thus it is to be expected that the phenyl group in Buna-S would give rise to absorption bands which would not be present in natural rubber, while conversely, the methyl groups of natural rubber would cause a characteristic absorption which would not be observed in Buna-S. Moreover, it is to be expected that there will be furhert bands characteristic of the molecule as a whole which will assist in the differentiation.

In the second place, so long as no intermolecular action occurs, the spectrum of a mixture of rubbers will be simply the spectra of the pure components combined in the proportion in which the materials themselves are present. Hence, it is to be expected that an unknown mixture can be analyzed by direct


NATURAL CREPE RUBBER
GUAYULE
NEOPRENE
BUNA-S
% TRANSMISSION
1800
1600
1400
1200
1000
800
FREQUENCY in cm.⁻¹


BUTYL RUBBER
THIOKOL B
HYCAR OR
PERBUNAN
% TRANSMISSION
1800
1600
1400
1200
1000
800
FREQUENCY in cm.⁻¹

measurement of the strength of absorption bands unique to each component, or by comparison of the absorption spectra of the unknown with those of a series of known prepared standards.

The infrared absorption spectra of various common types of rubber are shown in Figure 3[1]. The differences in these spectra readily show their applicability in identifying an unknown rubber or in estimating the content of a mixture. In the course of this investigation, only mixtures of natural rubber and Buna-S were encountered. A consideration of these two spectra in Figure 3 or Figure 4 shows several major points of difference—Buna-S has a strong aromatic ring frequency near 1500 cm.$^{-1}$ and two strong bands at 970 cm.$^{-1}$ and 917 cm.$^{-1}$ which are not present in the natural rubber. Natural rubber, on the other hand, shows a methyl band at 1380 cm.$^{-1}$ and a strong band at 835 cm.$^{-1}$ which are not observed in Buna-S. Taking advantage of these differences, each unknown sample was analyzed by comparison of its spectrum with the spectra of a series of known mixtures compounded and treated in approximately the same way as the unknown materials. The method is outlined roughly in Figure 4, showing the absorption spectra of natural rubber, 50% natural and 50% Buna-S, pure Buna-S, and an unknown tire tread. It can be seen from the 50–50 mixture that the unique bands mentioned above are all present with a strength proportional to the component concentration.

In the actual analysis, a great many intermediate standard spectra were obtained. An unknown was matched with one of this series by a comparison of the absorption intensities $\frac{1500 \text{ cm.}^{-1}}{1380 \text{ cm.}^{-1}}$ and $\frac{917 \text{ cm.}^{-1}}{835 \text{ cm.}^{-1}}$. By this method, an unknown such as that shown in Figure 4 could be estimated to be 85% natural rubber, 15% Buna-S. All absorption spectra were taken with samples smeared on salt plates and a high resolution spectrometer[8] was employed. The accuracy of the method is limited to 5 to 10% because of the inability to make smear samples of constant thickness. Greater accuracy, if desired, could be obtained by making percentage transmission measurements at the chosen frequencies according to some of the more involved analytical methods referred to above[9]. To justify the careful treatment, it would be necessary to study the unknowns and standards as solutions of known concentrations in a suitable solvent which would transmit infrared radiation at the analytical frequencies chosen. This more careful treatment would still require a preliminary complete absorption spectrum of each unknown to furnish a qualitative analysis for the various rubber materials which are present.

Sample preparation.—The methods described above are standard procedures and are given in detail in the references. Considerable time, however, had to be devoted to finding a means of converting a piece of tire stock to a sample whose infrared absorption spectrum could be measured. All attempts to obtain the spectra of the tire stocks directly, either by microtoming a thin section or by a smear from a solution of the stock material, were unsuccessful. To obtain a satisfactory spectrum, it is necessary to extract the rubber hydrocarbon free of plasticizer, filler, etc. The method finally devised was completely satisfactory for the authors' purpose, and should be of great value in any situation where it is desirable to separate filler and rubber without drestuction of the rubber hydrocarbon. Therefore, this separation by means of *p*-cymene and xylene solution is completely described below.

After this separation, the rubber is present as a solution in the hydrocarbon solvents. These solvents are removed by vacuum distillation until the rubber

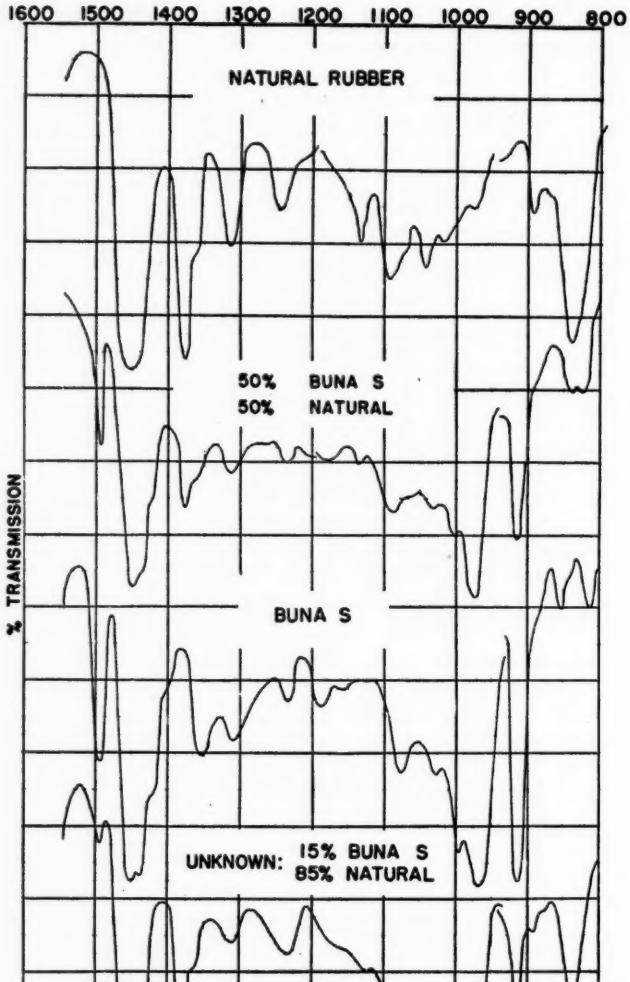


FIG. 4.—Outline of infrared analytical method. Spectra of prepared standards and unknown sample.

is a gummy solid that will not flow at room temperature. This gum is then washed four or five times with hot acetone to remove the last traces of plasticizer and solvent.

In most cases the state of the rubber is such that it can easily be smeared on a rock-salt plate. The desired thickness is obtained by scraping the film with a razor blade until the 1450 cm.$^{-1}$ CH band shows a transmission of about

10%. If the rubber does not spread easily, it may be softened with a volatile solvent such as carbon tetrachloride. The film is then dried in a vacuum oven to remove the last traces of solvent. Finally, the absorption spectrum of the sample is obtained throughout the spectral region of interest.

DISSOLVING RUBBER HYDROCARBON AND SEPARATING IT FROM COMPOUNDING INGREDIENTS

In the case of vulcanized natural rubber compositions, various solvent methods of determining the amount of rubber hydrocarbon have been used with some success. These methods, however, are somewhat involved and time-consuming. Even the A.S.T.M. method requires that the solution stand overinght to allow the mineral fillers and pigments to settle before filtration. If the rubber composition contains highly dispersed, exceedingly fine pigments, such as carbon black, separation of the pigments by filtration or centrifuging is usually impossible.

Since many present-day rubber products, particularly tire tread compositions or compounds, contain large amounts of carbon black, none of the above-mentioned methods appeared promising for separation of the rubber from the carbon black in suitable condition for infrared analysis. Accordingly, research on this question was nitiated.

Fearing that destruction or decomposition of the rubber hydrocarbons might reulst from the use of the conventional high-boiling solvents used in the above separation methods, a number of low-boiling solvents were tried: ethylene dichloride, toluene plus piperidine, *o*-nitroanisole, Dispersing Oil No. 10 (Barrett) plus xylene, and Circolight Process Oil (Sun Oil Co.) plus xylene. These experiments were unsuccessful.

Method I.—In the next attempts, which were somewhat more successful, xylene plus a small amount of thio-β-naphthol boiling under reflux was found to dissolve natural or synthetic tire tread stocks in 5 to 6 hours. To accomplish this, 1 gram of chloroform-acetone-extracted tread stock was heated in 100 cc. of xylene plus 0.3 gram of thio-β-naphthol at 140° C, until solution was complete.

However, this solution did not permit easy separation of the carbon black unless a combination of centrifuging and slight alcohol precipitation was used. (By adding alcohol to the solution, a small amount of rubber is precipitated to drag down the carbon black during centrifuging. There is some danger that this precipitation may be selective and thus change the composition of the residual rubber.) A sufficient separation of the carbon black can be made in this manner to permit fairly satisfactory infrared analysis. In the case of carcass stocks containing only zinc oxide as a filler, the pigment was easily separated by settling or centrifuging. This method was not completely satisfactory, however, because of carbon black troubles and the difficulty of removing the peptizer without loss of the rubber itself.

The search for a better means of carbon black separation was therefore continued. The cresol method[10] was tried with some success, although there was considerable oxidation of the rubber at the high reflux and distillation temperature required. The use of *p*-cymene in place of the cresol with digestion at about 160° to 170° C gave a satisfactory solution in about 4 hours and caused no noticeable oxidation of the rubber. On dilution with the benzene and 70° Bé rubber solvent gasoline, the supernatant liquid showed clearing in a few minutes and could be filtered free of the carbon black after standing

10 minutes. This method was further altered slightly by using 250 cc. of *n*-hexane instead of 300 cc. of 70° Bé gasoline for diluting the solution. Again the carbon black separated easily. To determine whether or not the same dilution technique would work with xylene as the solvent, a solution of the same tread stock was made with 30 cc. of xylene plus a small amount of thio-β-naphthol, but on diluting with benzene and hexane, the carbon black would not separate from the solution.

Further experiments showed that the combined use of *p*-cymene and xylene gave the most successful results and led to a satisfactory method.

TABLE III

COMPOSITION OF TYPICAL RUBBER STOCKS

	Stocks		
	87-1	A-912	A1-141
Smoked sheet rubber	50	100	...
Buna-S	50	...	100
Zinc oxide	50	5	5
Carbon black	...	50	50
Stearic acid	1	2.5	...
Pine tar	1.5	1.5	...
Thermoflex-A	...	1.4	...
Neozone-D	...	0.6	...
Bardol	...	...	5
Sulfur	2	3	2
Captax	...	1.2	1.5
Altax	1.25	...	...
Agerite Resin D	1.5	..	...

Method II (adopted for solution of rubber and separation of pigments).—Sheet the sample to a thickness of approximately 0.375 cm. (0.15 inch) on a tight cold 15 × 30 cm. (6 × 12 inch) laboratory mill.

Extract the plasticizer, etc., from 4 grams of the sheeted sample with a mixture of 32% by volume of acetone and 68% by volume of chloroform for a minimum of 7 hours, or until the extracting liquid no longer shows color. This size of sample is sufficient to permit repeat analyses.

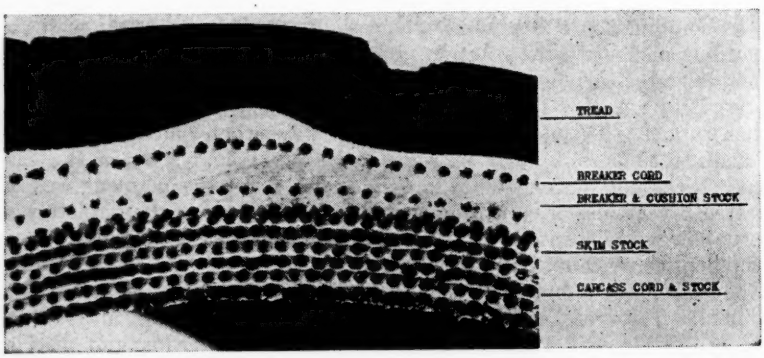


FIG. 5.—First step in sampling procedure. Labeled cross section of tire to be analyzed for rubber content.

Place 1.0 gram of the dried, extracted sample in a 400-cc. rubber extraction flask with 25 cc. of *p*-cymene and 5 cc. of xylene. Heat on a steam bath at about 70° to 80° C. for 1 hour, then on a hot plate under reflux at 150° to

160° C until the rubber stock is completely dissolved. Three to 4 hours are usually sufficient.

Cool and dilute with 20 cc. of benzene and then with 150 cc. of hexane. Allow the carbon black and other pigments to settle for at least 10 minutes, then decant the clear supernatant liquid through a No. 1 filter paper. If desired, filtration may be done with suction, using an asbestos pad.

Wash the flask, pigments, and filter with a mixture of 5 cc. of benzene and 45 cc. of hexane.

The above treatment easily removes the carbon black and other opaque compounding ingredients, giving a clear solution of the rubber from which the solvent may be removed by vacuum distillation.

TABLE IV

ANALYSIS OF CAPTURED GERMAN TIRES

Tire No.		Phosphorus (p.p.m.)	Infrared Natural (%)	Infrared Buna-S (%)
		Tread stocks		
FT	61	280	75	100	0
	99	30	0	0	100
	100	20	0	0	100
	101	10	0	0	100
	102	10	0	0	100
	103	30	0	0	100
	104	25	0	0	100
	105	20	0	0	100
	106	27	0	0	100
	107	3	0	0	100
		Carcass stocks		
FT	61	340	100	100	0
	99	340	100	100	0
	100	380	100	100	0
	101	430	100	100	0
	102	130	25	20	80
	103	190	50	50	50
	104	230	60	50	50
	105	200	50	80	20
	106	305	80	100	0
	107	190	50	50	50
		Cushion and tubes		
FT	61[a]	290	75	100	0
	99[a]	270	70	100	0
	101[a]	450	100	...	...
	102[b]	200	50	75	25
	103[b]	255	65	75	25
	104[b]	285	70	85	15
	105[b]	295	75	100	0
	106[b]	260	70	100	0
	107[b]	290	75	100	0

[a] Cushion [b] Tubes

To make valid comparisons between known and unknown samples, many mixtures of natural and Buna-S rubber in varying proportions were compounded according to the typical methods of preparing tread, carcass, and tube stocks. The rubber content of these known samples was then extracted according to the final method discussed above and was used for infrared comparison. The compounding ingredients used in three such typical standards are given in Table III. The infrared absorption spectrum of the 50–50 mixture is shown in Figure 4.

TYPICAL ANALYTICAL RESULTS ON ACTUAL TIRE AND TUBE STOCKS

This entire project was initiated to provide a suitable method for determining the composition of tires and tubes, with particular reference to the types and relative amounts of the various rubbers present. The analytical methods which were evolved were applied successfully to a large number of samples. The type of information obtained is well illustrated by the results shown below, which were selected at random from the samples examined.

The tires, when received, were cross-sectioned, photographed, and labeled as shown in Figure 5, thus ensuring a permanent record of the tires and a ready means of identifying the various samples chosen. Wherever possible, samples of the tread, cushion, breaker, and carcass stocks were removed from each tire, extracted, prepared for study, and then subjected to the two analytical procedures.

In Table IV, the results obtained on a few typical German tires and inner tubes are presented. In view of the spread in the phosphorus contents of natural rubbers from various sources (Table II), a mean value of 400 p.p.m. was used in making the analytical calculations from phosphorus determinations. The agreement between the infrared and the phosphorus methods is therefore all the more gratifying.

SUMMARY

In a compounded rubber stock, the ratio of natural to synthetic rubber can be estimated approximately from a knowledge of the phosphorus content of the rubber hydrocarbon. A considerably more exact analysis can be carried out by infrared spectroscopic methods, which permit a determination of the type as well as the amount of rubber present. Complete details and comparative results of these two methods of analysis are given, as well as a simple procedure for separating the rubber hydrocarbon of a rubber stock from carbon black and other compounding ingredients.

ACKNOWLEDGMENT

In conclusion, the authors would like to express their appreciation to the several other members of the staff of this laboratory who helped materially in the establishment of these analytical methods.

REFERENCES

[1] Barnes, Liddel, and Williams, *Ind. Eng. Chem., Anal. Ed.* **15**, 83 (1943).
[2] Zinzadze, *Ind. Eng. Chem., Anal. Ed.* **7**, 227 (1935).
[3] Goodloe, *Ind. Eng. Chem., Anal. Ed.* **9**, 527 (1935).
[4] Clibbens and Gaeke, *J. Textile Inst.* **19**, 77 (1928).
[5] Carver, Bingham, Bradshaw and Venable, *Ind. Eng. Chem., Anal. Ed.* **1**, 49 (1929).
[6] Kuttner and Cohen, *J. Biol. Chem.* **75**, 517 (1927).
[7] Barnes, Liddel and Williams, *Ind. Eng. Chem., Anal. Ed.* **15**, 83, 659 (1943); Brattain, Rasmussen and Cravath, *J. Applied Physics* **14**, 418 (1943); Nielsen and Smith, *Ind. Eng. Chem., Anal. Ed.* **15**, 609 (1943).
[8] Barnes, Liddel and Williams, *Ind. Eng. Chem., Anal. Ed.* **15**, 83 (1943).
[9] Barnes, Liddel and Williams, *Ind. Eng. Chem., Anal. Ed.* **15**, 83 (1943); Brattain, Rasmussen and Cravath, *J. Applied Physics* **14**, 418 (1943); Nielsen and Smith, *Ind. Eng. Chem., Anal. Ed.* **15**, 609 (1943).
[10] Roberts, RUBBER CHEM. TECH. **14**, 241 (1941).

THE COURSE OF AUTOÖXIDATION REACTIONS IN POLYISOPRENE AND ALLIED COMPOUNDS

III. THE OXIDATION OF RUBBER IN THE PRESENCE OF ACETIC ACID OR ACETIC ANHYDRIDE

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Reference has been made in Part I of this series[1] to the ready oxidation which occurs when rubber is exposed to oxygen in the presence of boiling acetic anhydride. It might at first be suspected that oxidation is here greatly facilitated by destruction of the natural inhibitors present in the rubber by the acid medium employed[2], but if this were the sole explanation of this rapid oxidation, then a sample of rubber from which the antioxidants had been removed by acetone extraction[3] would be expected to undergo oxidation in a neutral or alkaline medium at a rate comparable with that observed in the acidic medium, although the course of the secondary reactions, and hence the final products of oxidation, might well be considerably different in view of the diverse influence of acid and alkali on the mode of decay of the hydroperoxide of cyclohexene[1].

Bloomfield and Farmer[4] first observed that the oxidation of olefins by oxygen can be much accelerated by the presence of acetic acid or anhydride, and similar observations by other authors have since been reported. If in these reactions autoöxidation proceeds by addition of oxygen at the unsaturated centers of rubber to give peroxide groups $\begin{matrix}-C-C-\\ |\ \ |\\ O-O\end{matrix}$ according to the Engler-Bach hypothesis, it might be supposed that ultimately there would be formed partly or wholly acetylated diols by reason of the decay of the peroxides in the presence of acetic acid or acetic anhydride. If, however, oxidative attack is directed in the first place to the α-methylene carbon atoms instead of to the unsaturated centers, tri-, di-, or mono-acetylated triol groups may be expected to arise at each $CH_2 \cdot C:C$ unit, as already discussed[1].

The oxidation process.—At ordinary temperatures the oxidation of solid rubber took place quite slowly when the hydrocarbon was immersed in acetic anhydride or acetic acid, but at 120–140° oxidation proceeded rapidly, and the products of oxidation were sufficiently degraded to dissolve in hot acetic acid or anhydride, giving a resinous material which by submission to a suitable separative procedure (see Tables III and IV) could be resolved into various fractions of high oxygen contents and of comparatively low molecular weights. The undissolved rubber, on the other hand, although somewhat softer than it was originally, was only slightly oxygenated and but little degraded. The reaction could be considerably accelerated by adding small proportions of organic or inorganic cobalt salts to the acid or anhydride medium, but no obvious change in the course of reaction attended these additions.

It was hoped to bring about more regulated oxidation, and so to obtain more graded oxidation products, by bringing the rubber to reaction in solution, but in fact no significant oxidation occurred unless rubber recovered from one of the above oxidations conducted in the presence of acetic anhydride or acetic acid, and so already slightly oxidized, was used in place of fresh rubber, or unless the oxidation was started, but not indefinitely continued, in a medium relatively poor in hydrocarbon solvent. Even under these modified conditions, oxidation did not proceed beyond the incorporation of a few units per cent of oxygen unless the solution was irradiated or an organic salt of cobalt was added as a catalyst. In the latter case reaction proceeded to an advanced stage, with formation of highly oxygenated products which, for all oxidations conducted in the presence of acetic anhydride, were very similar to those obtained in the absence of a solvent for the rubber. When, however, oxidation was accelerated by irradiation, the reaction appeared to pursue a somewhat different course, since then rather less than one-half of the combined oxygen was found in acetoxyl groups.

It was necessary, before proceeding further with the examination of the oxidation products formed in presence of acetic acid or its anhydride, to ensure that no serious part of the oxygenation of rubber arose by the direct addition of acetic acid at the ethylenic centers of the hydrocarbon (cf. addition of acetic or di- or trichloroacetic acid to amylene[5]). Accordingly, samples of rubber were treated for many hours with boiling acetic anhydride and others with boiling acetic acid, in an atmosphere of carefully purified nitrogen. Under these conditions no combination of the rubber with either reagent could be detected. Furthermore, when rubber was sealed in an evacuated tube together with acetic anhydride and sufficient benzene to promote considerable dissolution of the rubber, it was recovered substantially unchanged even after many hours' heating at 140°.

The main features therefore of the reaction under consideration are: (1) rubber takes up substantial amounts of oxygen in the presence of acetic acid or anhydride, but the reaction is very slow and restricted in character unless a temperature well above 100° is used; (2) the rubber becomes increasingly degraded as the oxygen content of the product rises; and (3) only a portion of the oxygen incorporated is in the form of acetoxyl groups, especially where the presence of a hydrocarbon diluent causes the acetic acid or anhydride to be in low concentration.

The constitution of the highly degraded products.—Further study of the major reaction products obtained severally by use of undiluted acetic anhydride and acetic acid at 120–140° (products A and P) showed that acetoxyl contents as high as 50 per cent could be obtained without entire removal of the unsaturation of the rubber; the magnitude of the acetoxyl contents in the acetic anhydride products arising at similar stages of oxygenation appeared to be mainly a function of the freedom of the anhydride from acetic acid, and acetic acid alone gave products of lowest acetoxyl content.

The products were nonperoxidic, acid substances (containing titratable carboxyl groups) and for the most part showed a significant content of unesterified hydroxyl groups. The chief analytical characteristics are given in Table I (blank spaces represent undetermined values).

There is a discrepancy (average 2.7%) between the total oxygen content of the products determined by elementary analysis and by summation of the acetoxyl, carboxyl, and hydroxyl oxygen. This is to be expected, since the scission of polyisoprene chains at the double bonds by autoöxidation reactions

normally gives rise to carbonyl groupings[1]. Direct determination of the carbonyl content in two examples [A(i)5 and P(i)3] gave values (3.9 and 6.4%) which were actually in excess of this difference. In the determination of hydroxyl contents by the precision method of Bolland[6], the usual vigorous evolution of methane was accompanied by a progressive slow evolution of gas, possibly due to enolization of carbonyl groups, and the hydroxyl contents in Table I have been derived by neglecting the slow reaction [A(i)3 excepted].

TABLE I

HIGHLY OXIDIZED PRODUCTS

Product	Medium	Catalyst	OAc (%) (corr.)*	CO_2H (%) (corr.)*	OH (%)	I.V.	*M*	Analysis (%) C	H	O (diff.)	O content (OAc + CO_2H + OH)
A(i)	Ac_2O	None	50.5	6.0	...	49	...	59.85	6.9	33.25	31.7
A(ii)	"	"	44.0	4.0	...	...	...	63.1	7.4	29.5	26.7
A(i)2	"	"	55.0†	7.1†	...	...	...	...	...	...	...
A(i)3	"	"	42.2	5.7	2.5 *ca.*	80	...	64.0	6.9	29.1	29.3
A(i)5	"	"	44.1	8.0	nil	71	716	61.1	6.9	32.0	29.6
A(i)6	"	$Co(NO_3)_2$	39.6	6.0	nil	77	1143	63.9	6.9	29.2	25.8
A(i)7	"	"	47.3	5.4	0.3	71	1215	62.7	6.9	30.4	29.8
A(i)8	$C_6H_6 + Ac_2O$	CoL_2‡	36.8	6.0	0.3	91	1361	61.8	7.2	31.0	24.6
A(i)9	$C_6H_5Cl + Ac_2O$	None	36.1	6.3	4.0	90	1161	63.9	7.0	29.1	27.9
P(i)	AcOH	"	33.2	8.2	3.0	98	...	62.2	7.25	30.55	26.6
P(i)2	"	"	31.8	5.6	5.2	...	...	63.6	7.4	29.0	26.2
P(i)3	"	"	27.8	7.8	4.1	90.5	...	63.6	7.3	29.1	24.5

* For the significance of the correction applied to these figures, see later.
† Uncorrected value.
‡ Cobalt linoleate.

Most of the molecular weights shown are to be regarded as maximum values, since the solubility of the products in benzene decreased after a time, and only in the case of A(i)5 was it possible to determine the molecular weight immediately after preparation. Saponification of the acetylated substances under conditions excluding any possibility of further oxidation resulted in decomposition of the acetoxyl groups and formation of additional hydroxyl groups. In Table II are given analytical details for the saponification products of six of the materials listed in Table I.

TABLE II

COMPOSITION OF SAPONIFICATION PRODUCTS

Products from which derived	I.V.	OH (%)	CO_2H (%)	C (%)	H (%)	O (%)
A(i)3 (42.2% OAc)	112	18	8.1	68.3	7.5	24.2
A(i)5 (44.0% OAc)	124	12.4	11.6	66.4	7.6	26.0
A(i)7 (47.3% OAc)	114	20	8.2	67.5	7.6	24.9
A(i)9 (36.1% OAc)	167	13.5	8.5	68.8	7.8	23.4
P(i)2 (31.8% OAc)	...	11.0	7.3	67.1	7.4	25.5
P(i)3 (27.8% OAc)	143	11.7	9.9	69.4	7.8	22.8

The presence of many free hydroxyl groups in the saponified substances appears to lead to considerable dehydration, possibly by lactone formation (largely intramolecular) with the carboxyl groups already present: not only were the hydroxyl contents much lower than were to be expected, but titration of the acid groups gave satisfactorily sharp end-points only when the substances were treated with excess of alkali and back-titrated. The carboxyl contents of the hydroxy acids were somewhat greater than those calculated from the apparent carboxyl content of the parent acetylated substances, and this was to be expected, since it was not possible to determine the carboxyl contents of the latter with very high precision, because of the presence of readily hydrolyzable acetoxyl groups. The discrepancy was not generally large, and an appropriate correction has been applied to the carboxyl contents

of the acetylated substances in Table I. The application of this correction also involved a small correction to the acetoxyl contents. The compositions of the saponified substances derived from products of high acetoxyl content are in fairly good agreement with those calculated from the composition of the parent acetylated substances on the assumption that lactonic elimination of water between the carboxyl groups and a corresponding proportion of the hydroxyl groups has occurred, but there is less agreement in the materials originally of lower acetoxyl content, owing possibly to some lactonization already present between carboxyl groups and free hydroxyl groups in the acetylated substance.

When an attempt was made to divert secondary reaction along a different route by an alkaline auxiliary reagent (alcoholic potassium hydroxide) in place of the acid ones used before, no significant oxidation occurred at temperatures in the neighborhood of 80–100°, and even at 140° only 3 per cent of combined oxygen was introduced after 64 hours, but an oxidation conducted in the presence of pyridine proceeded to a more advanced stage represented by the combination of 8.6 per cent of oxygen, of which, however, only one-third appeared in the form of hydroxyl, carbonyl, and carboxyl groups. As in the case of acid auxiliary reagents, considerable molecular degradation occurred.

Mechanism of the reaction.—Before considering the acetoxyl content in relation to the residual unsaturation of the highly oxygenated products, it is necessary to take into account chain scission, since the extent of degradation occurring during oxidation is such that end-groups must constitute an appreciable part of the molecule. Indeed, the observed orders of magnitude of the carbonyl and carboxyl contents are just such as would be expected to characterize chain scission products of molecular weight 700–1000, in which the groupings in question are confined to the ends of chains.

The autoöxidation reaction now under consideration differs from that described earlier[1] in being thermal rather than mainly photochemical in character. Hence the course followed (and this applies especially to secondary reaction) may be very different from that previously discussed. If it be assumed, however, that oxidation necessarily consists at the first stage of the absorption of molecular oxygen in giving not merely peroxide groups but hydroperoxide groups, and that the decomposition of these, instead of following the ordinary thermal or photochemical course, is directly influenced by the presence of an auxiliary reagent (acetic anhydride, etc.), it becomes possible to make important comparisons between the observed and the expected character of the reaction products. It is obvious that, in any particular oxidation, the participation of the auxiliary reagent may be belated or for one cause or another fall short of completeness, and in this case the secondary reactions comprise both normal thermal peroxidic degradations and "influenced" degradations. Also it may reasonably be assumed, since there is as yet no evidence to the contrary in any recorded autoöxidation, that the oxidizing power of the peroxide groups expends itself primarily in attacking the unsaturated centers in the molecule where such are present, so giving rise to chain-scission. The normal molecular form of the reaction products may accordingly be expected to be some oxygenated and acetoxylated modification of (I), in which $n < 6$, in which the most probable points of hydroperoxidation are at the asterisked carbon atoms.

Some of the inner isoprene units in the small fragments of the original rubber chains will have escaped reaction altogether, others in the main will (as indicated in Part I[1]) have passed in the presence of acetic anhydride into

acetoxylated units containing in all probability the systems (II) or (III), or to some extent (especially where the oxidation is conducted in the presence of acetic acid) the systems (IV) or (V). There does indeed appear to be one free hydroxyl group for every two acetoxyl groups in the oxidation products of higher hydroxyl content as the figures below indicate:

Product	A(i)9	P(i)	P(i)2	P(i)3
OH equivalent of OAc content (%)	10.4	9.6	9.2	8.0
Free OH content (%)	4.0	3.0	5.2	4.1

In the most highly acetylated products, the acetoxyl content can be related to the iodine value without any complication arising from the presence of free hydroxyl groups, and these products conform closely with the structural type represented by (I). For instance, a substance (VI) requires C, 60.0; H, 7.45; OAc, 47.8; CO, 3.8; CO_2H, 6.1%; I. V., 69; *M*, 740 [cf. A(i)5 and A(i)7],

$$\overset{*}{CO_2H}\cdot CH_2\cdot [CH_2\cdot CMe{:}CH\cdot CH_2]_n\cdot CH_2\cdot \overset{*}{COMe}$$
(I)

$$—CH(OAc)\cdot CMe(OAc)\cdot CH(OAc)\cdot CH_2—$$
(II)

$$—CH_2\cdot CMe(OAc)\cdot CH(OAc)\cdot CH(OAc)—$$
(III)

$$—CH(OH)\cdot CMe(OAc)\cdot CH(OAc)\cdot CH_2—$$
(IV)

$$—CH_2\cdot CMe(OAc)\cdot CH(OAc)\cdot CH(OH)—$$
(V)

$$CO_2H\cdot CH_2\cdot [CH(OAc)\cdot CMe(OAc)\cdot CH(OAc)\cdot CH_2]_2\cdot [CH_2\cdot CMe{:}CH\cdot CH_2]_2\cdot CH_2\cdot COMe$$
(VI)

$$CO_2H\cdot CH_2\cdot [CH_2\cdot CMe(OAc)\cdot CH(OAc)\cdot CH_2]_3\cdot CH_2\cdot CMe{:}CH\cdot CH_2\cdot CH_2\cdot COMe$$
(VII)

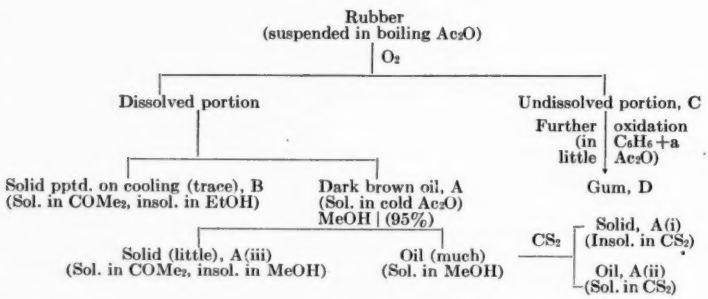
whereas the alternative mode of distribution of the acetoxyl groups in a substance such as (VII), in which no α-methylene hydroperoxidation has taken place, so limiting the attachment of acetoxyl groups to two in each C_5H_8 unit attacked, would require a considerably lower iodine value (34) if the acetoxyl content is to remain the same.

EXPERIMENTAL

Oxidation of rubber in boiling acetic acid or acetic anhydride.—The rubber (20 g.) was immersed in acetic acid or acetic anhydride (200 cc.), which was boiled under reflux while a brisk stream of oxygen was bubbled through. The pieces of rubber disintegrated, and a portion dissolved to a dark brown solution. After at least 20 hours' treatment, the hot solution was decanted from a small amount of undissolved rubber. The solution, on cooling, deposited a little resinous material. The material remaining in solution was isolated by

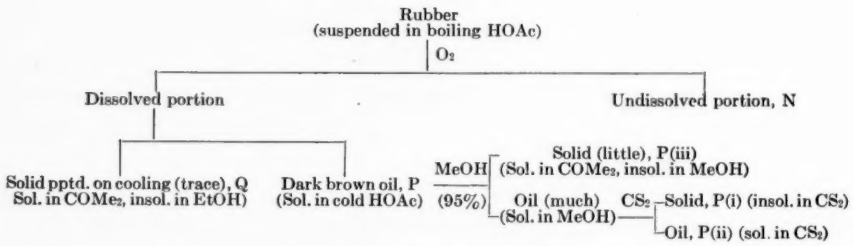
evaporation of the acetic acid or anhydride under reduced pressure, the residue being submitted to the separative procedure indicated in Table III.

TABLE III



In oxidations conducted in acetic anhydride, the yield of the brown solid product A(i) was about the same as that of the oil A(ii), the resinous products B and A(iii) being formed in relatively small amount. The solid A(i) softened at about 50°, and melted to a gum at somewhat higher temperatures; a portion of the oil A(ii) was sufficiently degraded to be volatile at about 0.1 mm. pressure. When the oxidations were conducted in acetic acid, the amount of the corresponding products [solid P(i) and oil P(ii): see Table IV] were reduced, and the oil P(ii) was formed in greater amount than the solid P(i).

TABLE IV



When cobalt nitrate (0.4 g.) was added to the acetic acid or anhydride, the amount of rubber which dissolved in a comparable time was greater than in the absence of catalyst, but the products were very similar. The yield of the solid reaction product was, however, much greater than that of the oil, and in a typical experiment 29.6 g. of a solid reaction product [A(i)6] were obtained from 30 g. of rubber. Complete removal of the cobalt salts from the reaction products presented much difficulty.

Oxidation of rubber in acetic acid or anhydride, using a supplementary solvent.—Oxygen was first led for 40 hours into a solution of rubber (10 g.) in benzene (500 cc.) containing acetic anhydride (50 cc.), a temperature of 80° being maintained. No significant degree of oxidation occurred. A similar result was obtained when an isopropyl acetate-acetic anhydride medium (at 90°) was used. When, however, a sample of the slightly degraded product C (found: C, 88.0; H, 11.7%) was dissolved in benzene containing a little acetic anhydride, some evidence of oxidative attack became apparent after oxygen had been passed for 10 hours at 80°. The solution was then much less viscous,

and removal of the solvent at this stage yielded a brown gum D, which was soluble in warm ethyl acetate, ether, hydrocarbon solvents, methylethyl ketone, and dioxan, but insoluble in alcohol or acetone (found: C, 85.8; H, 11.6; OAC, *ca.* 2%).

Product D was soluble in a mixture of benzene (2 vols.) and acetic anhydride (1 vol.), but an oxidation of rubber attempted in this mixture proceeded only very slowly. When, however, the rubber (10 g.) was placed in a mixture of benzene (50 cc.) and acetic anhydride (50 cc.) and heated at 80° in contact with a stream of oxygen for 12 hours, and afterwards fruther benzene (50 cc.) was added, all of the rubber dissolved in the course of a further 8 hours' treatment with oxygen at 80°, giving a solution of low viscosity. Removal of solvents gave a pale yellow, turbid gum behaving similarly to the material D towards solvents. When a solution of this new product in light petroleum (1000 cc.) was allowed to stand, a pale yellow powder (0.2 g.) separated: this was removed by centrifuging and washed with light petroleum (found: N, 9.4%). The resulting clear solution yielded, on evaporation of the solvent, a clear transparent pale yellow gum J {found: C, 87.0; H, 11.8; N, nil; OAc, 0.86%; I. V., 353; intrinsic viscosity [η] (in benzene + 15% methanol), 0.244, from which M = 25,000}. In another oxidation conducted under similar conditions but using a mixture of equal volumes of acetic acid and anhydride a product K, very similar to J, was obtained {found: C, 87.5; H, 11.95; OAc, 0.54%; I. V., 362; [η] (in benzene + 15% methanol), 0.354, from which M = 36,000}, but when only acetic acid in admixture with the same proportion of benzene was used, a tacky, rubberlike substance L resulted {found: C, 87.85; H, 11.9; OAc, nil; [η] (in benzene), 1.59, from which M = 95,000}[7].

Use of a catalyst.—Oxidations were conducted under similar conditions to those described in the preceding paragraph with the addition of cobalt linoleate (0.2 g. per 10 g. of rubber). When a mixture of acetic acid, acetic anhydride, and benzene was treated with oxygen in the presence of this catalyst (at 80°), the product was very similar to that obtained from rubber, acetic anhydride, and oxygen at 140°. Like the latter product, it was divided into solid A(i)8 (10 g.) and liquid (3 g.) fractions which were respectively insoluble and soluble in carbon disulfide. Replacement of the acid-anhydride mixture by acetic acid alone led under the same conditions of oxidation to the formation of a less highly oxidized product, which by selective dissolution yielded the following fractions: alcohol-soluble portion, 3 g. (found: C, 71.8; H, 9.2; OAc, 14.0; CO_2H, 4.0%); acetone-soluble portion, 3.0 g. (found: C, 79.7; H, 10.4; OAc, 10.6; CO_2H, 1.5%); petroleum-soluble, acetone-insoluble portion, 3.6 g. (found: C, 81.7; H, 10.9; OAc, 4.6%).

Oxidation in presence of a mutual (high-boiling) solvent for the reactants.—Rubber (10 g.) was swollen in chlorobenzene (100 cc.), acetic anhydride (150 cc.) added, and the mixture heated during 40 hours at 140°, while a brisk current of oxygen was passed through. The separative procedure indicated in Table III was applied to the highly oxygenated product, and fractions severally soluble (oil, 5.4 g.) and insoluble [solid A(i)9, 3.4 g.] in carbon disulfide were isolated. When the anhydride was replaced by acetic acid, the oxidation followed a different course, and yielded a gum wholly soluble in light petroleum and in carbon disulfide, but insoluble in alcohol and in acetone.

Oxidation in presence of acetic anhydride, with irradiation.—A solution of acetic anhydride (25 cc.) in benzene (50 cc.) did not absorb oxygen when exposed at 30–40° in a Pyrex flask for 4 hours to ultraviolet light (Hanovia U.V.S. 500); moreover, the solution contained thereafter only a trace of perox-

idic material. Accordingly, rubber (10 g.) in benzene (50 cc.) and acetic anhydride (50 cc.) was submitted to the action of oxygen at 80° until dissolved (cf. preceding experiments). Further benzene was then added, and the solution was oxidized at 30–40° under radiation as above for 16 hours. The solution, which had absorbed altogether 1,800 cc. of oxygen, was concentrated under reduced pressure, and the gummy product isolated by pouring the concentrate into alcohol and removing the residual solvent in a high vacuum (found: C, 68.2; H, 9.15; OAc, 20.0; peroxidic oxygen, *ca.* 1%; equiv., 2060; I. V., 210).

Saponification of highly acetylated products.—To a solution of the acetylated material in the minimum quantity of 95% ethyl alcohol was added 2% aqueous sodium hydroxide (100 cc. per g. of substance). The solution was boiled under reflux for 6 hours in an atmosphere of nitrogen, a little benzene being added to suppress frothing. The bulk of the solution was reduced considerably by evaporation under reduced pressure, and the remainder was acidified, whereupon the hydrolysis product was precipitated as a sludge, which was separated and washed on the centrifuge. In the later stages of washing, the product readily passed into colloidal solution in water unless a few drops of a dilute acid were added. The product was rapidly dried at room temperature and reduced pressure, redissolved in alcohol, and separated from silica. The alcohol was finally removed at room temperature, yielding a friable solid, insoluble in hydrocarbons, readily soluble in alcohol, acetone, acetic acid, and pyridine. The yield was almost quantitative provided that care were exercised to prevent losses while washing the precipitate.

Oxidation in the presence of chloroacetic acid.—The rubber (20 g.) was placed in molten chloroacetic acid (200 cc.) maintained at 140° while a stream of oxygen was passed through for 50 hours. The bulk of the rubber remained undissolved, but appeared to have undergone some change since, after being extracted with acetone to remove residual chloroacetic acid, it was recovered as a tough, nonelastic, insoluble mass. The chloroacetic acid itself, decanted from the afore-mentioned insoluble matter, was very dark, and yielded a brown precipitate on being poured into water. The dried precipitate (1.8 g.) (found: Cl, 2.9%) was sparingly soluble in alcohol and in acetone, insoluble in benzene, carbon disulfide, and ethyl acetate, but readily soluble in benzene-acetone.

Attempted oxidation in alkaline media.—Rubber (20 g.) was placed in 0.5 *N* alcoholic potassium hydroxide (300 cc.) and heated at 80° while oxygen was passed through the solution for 40 hours. No rubber dissolved during this time, and the recovered rubber contained very little oxygen (found: C, 87.6; H, 11.7%); this was next placed in benzene (300 cc.) containing 100 cc. of 0.5 *N* alcoholic potassium hydroxide, and the oxidation resumed at 80°. After 30 hours no extensive degree of oxidation had occurred (found: C, 87.3; H, 11.7%). Rubber (10 g.) in pyridine (100 cc.) was submitted to the action of oxygen at 100°. The rubber passed into solution, and after continuation of the treatment for 40 hours, the pyridine was removed under reduced pressure. The residue was treated with warm aqueous hydrochloric acid (2 *N*), taken up in ether, and this solution was well washed and dried. Removal of the ether yielded a dark brown gum {found: C, 80.7; H, 10.7; N, trace; OH (including OH in CO_2H groups), 2.0%; CO + CHO, equivalent to 1% oxygen; equiv., 3,600; $[\eta]$ (in benzene + 15% methanol), 0.095, from which $M = 7{,}900$}.

Analytical methods.—*Acidity* was determined by titration of a dilute solution of the sample (0.1 g.) in aqueous alcohol (100 cc.) with 0.1 *N* sodium

hydroxide, phenolphthalein being the indicator. The high dilution was necessary so that the color of the solution should not mask the end point. The *acetoxyl content* of materials of small total oxygen content was determined by dissolving the sample (0.5–1.0 g.) in benzene, adding alcoholic potassium hydroxide, and refluxing the mixture for 4–6 hours in an atmosphere of nitrogen. For highly oxygenated materials, 0.1 g. was dissolved in 95% ethanol (10 cc.), 25 cc. of 0.2 *N* potassium hydroxide (aqueous) were added, and the solution was boiled for at least 4 hours in an atmosphere of nitrogen under a reflux condenser guarded by a soda-lime tube. From the alkali consumed was deducted the amount required to neutralize the acidity of the sample. The *iodine values* were determined by the Kemp-Wijs method[8]; the oxidation products did not give a reaction for peroxidic oxygen, and hence did not liberate iodine from potassium iodide. *Molecular weights* of the highly oxygenated materials were determined cryoscopically in benzene, and *hydroxyl contents* of materials soluble in benzene, toluene, or anisole by Bolland's method[6]. The highly hydroxylated products were not soluble in the foregoing solvents, and accordingly pyridine was used with a slight modification to Bolland's procedure, since the Grignard pyridine complex appeared to be slightly volatile in a high vacuum. This modification involved placing a stopcock in the tube connecting the two limbs of the reaction vessel, and thereafter distilling the pyridine contained (together with a little methyl-magnesium iodide) in the right-hand limb on to the sample in the other limb. Later, the stopcock was closed, and further reagent (in toluene) introduced into the right-hand limb. After the usual preliminary degassing, the stopcock was reopened, and the reagent allowed to flow on to the sample. After this point the normal procedure was followed. If there was any premature reaction with traces of the reagent which had volatilized with the pyridine, the methane so produced was confined in the closed limb of the reaction vessel and was not lost in the preliminary degassing operations.

SUMMARY

Oxidation of rubber by oxygen in the presence of acetic anhydride leads to formation of highly oxygenated products containing a considerable proportion of acetoxyl groups. The residual unsaturation of the products of highest acetoxyl content, taken in conjunction with other analytical characteristics, indicates that three, rather than two, acetoxyl groups normally combine with each isoprene unit attacked. Although the bulk of the oxygen introduced is present in the form of acetoxyl groups, a portion occurs as carboxyl and carbonyl groups; also, whenever acetic acid is used (partly or wholly) in place of acetic anhydride, some free hydroxyl groups appear in the oxidized rubber. The proportions of carboxyl and carbonyl groups observed can be correlated satisfactorily with the extent of chain-scission occurring during the oxidation, the groups in question forming the new ends of the severed molecules. Hydrolysis of the acetylated products yields hydroxy acids, which readily undergo lactonic elimination of water.

Acetic anhydride and acetic acid can clearly act as auxiliary reagents in autoöxidation reactions, and the detailed results obtained with rubber can be best accounted for on the basis of α-methylene peroxidation, followed by decay reactions involving incorporation of the auxiliary reagent as well as oxidative attack at the double bonds of the rubber.

ACKNOWLEDGMENT

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REFERENCES

[1] Bloomfield, *J. Chem. Soc.*, **1942**, 121.
[2] Bruson, Sebrell and Vogt, *Ind. Eng. Chem.* **19**, 1187 (1927).
[3] In the following pages, unless otherwise specifically indicated, the term rubber means acetone-extracted crepe rubber.
[4] Bloomfield and Farmer, *J. Soc. Chem. Ind.* **54**, 125T (1935).
[5] Konovalov, *Z. physik. Chem.* **2**, 380 (1888); Nernst and Hohmann, *Z. physik. Chem.* **11**, 352 (1893).
[6] Bolland, *Trans. Inst. Rubber Ind.* **16**, 267 (1941).
[7] The original paper had M (determined by viscosity) approximately 300,000. These molecular weights have been determined by G. Gee, to whom the author's thanks are due.
[8] Kemp and Mueller, *Ind. Eng. Chem., Anal. Ed.* **6**, 52 (1934).

RUBBER, POLYISOPRENES AND ALLIED COMPOUNDS

V. THE CHEMICAL LINKING OF RUBBER AND OF OTHER OLEFINS WITH PHENOL–FORMALDEHYDE RESINS *

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Rubber combines readily with maleic anhydride up to a limit of one molecule of the latter per isoprene unit of the former[1]. The comparative ease of occurrence of this reaction made it seem feasible to use maleic and similar unsaturated anhydrides (or acids) as a means of linking rubber chemically with various types of hydroxylic compound, the ethylenic carbon pairs of the maleic molecules serving to form C—C links with the rubber, and the anhydro groupings to form ester links with hydroxy compounds. Although it was possible to carry out this linking process successfully in a number of examples, the combination of rubber with phenol-formaldehyde resins could be much more satisfactorily effected if the rubber-maleic anhydride compound was not preformed, but, instead, a somewhat oxidized rubber together with maleic anhydride, phenol, and formaldehyde were simply heated together until resin formation occurred[2]. Subsequently, it was found that considerably oxidized rubber (oxygen, approximately 10–13%; M, 3000–4000) reacted more readily than slightly oxidized rubber, the product being a thermosetting resin of Bakelite type, remarkable in possessing valuable residual thermoplastic properties. Investigation of the chemical reaction by which this resin is produced has given rather unexpected results in the field of additive reactions, and has thrown new light on the process of resinification.

It was soon discovered that maleic anhydride could be satisfactorily replaced by oxalic or acetic acid, and no evidence could be gained that any appreciable degree of esterification of the anhydride units by the hydroxylic phenol-formaldehyde components occurred. Hence the maleic anhydride clearly functioned largely as a mild acid catalyst. The great improvement in the ease of condensation which followed the replacement of lightly oxidized by considerably oxidized rubber seemed at first to indicate that a reaction of aldol type took place between the ·CHO or ·COMe end-groups of the shortened rubber chains and the keto-tautomer of phenol or, alternatively, that elimination of water occurred between hydroxyl groups in the oxidized rubber and the aromatic nuclei of the phenol. Thorough experimental examination, however, of these possibilities led to their dismissal from further consideration (the experimental details have been omitted). There remained, then, no very reasonable alternative to the conclusion that rubber and, therefore, probably most olefinic substances, are able, in virtue of their olefinic unsaturation, to combine with phenol and formaldehyde at some stage in the intercondensation of the latter, and this conclusion was reënforced by certain experiments carried

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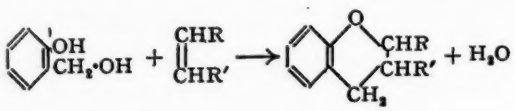
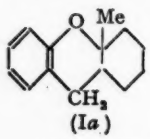
out by Hilditch and Smith[3] in 1935, which strongly indicate that drying-oil esters are able because of their unsaturation to combine with a simple *p*-cresol-formaldehyde condensation product. Any remaining doubt as to the capacity of olefinic materials to unite or condense with simple phenol-formaldehyde condensation products was removed by the publication at this point of a paper by Hultzsch[4], in which the result of heating saligenin with styrene was reported

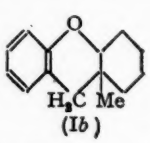


to be the formation of 2-phenylchroman, and that of heating several other simple phenol-formaldehyde condensation products containing ·OH and ·CH_2·OH groups in *o*-positions with olefinic alcohols, esters, etc., was the formation of analogous chroman derivatives. Curiously enough, however, cyclohexene was reported not to undergo condensation with saligenin.

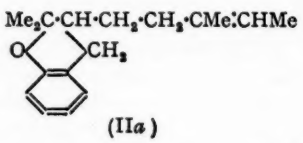
We found on examining the behavior towards saligenin of the two simple analogs of rubber, 1-methyl-cyclohexene and dihydromyrcene, that reaction in each case occurs readily at 180°, giving by loss of water a nonhydroxylic, oxygen-containing condensation product having the general properties and empirical composition to be expected for chroman structures of the type reported by Hultzsch[4]. The diolefin, dihydromyrcene, however, formed a di- as well as a monosaligenino-condensation product, the two compounds resembling one another in containing no active hydrogen, but differing in containing respectively no hydrogenizable double bond, and one such bond. For the compound from 1-methylcyclohexene, (I*a*) and (I*b*) are possible formulas, but



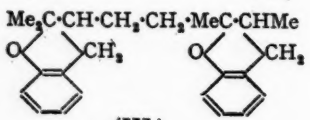
(I*a*)



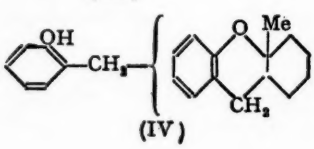
(I*b*)



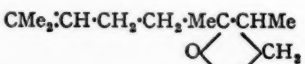
(II*a*)



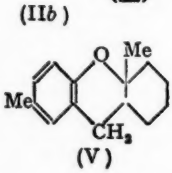
(III)



(IV)



(II*b*)



(V)

since any addition of a reagent to an unsymmetrical olefin CRR′:CH_2 or CRR′:CHR″ normally proceeds almost entirely in one direction (as deter-

mined by the relative polarity of the ethylenic carbon atoms) (I*b*) is unlikely to represent any considerable proportion of the product unless the addition reaction involves radical forms (see below). Similarly, for the two compounds from dihydromyrcene the monosaligenin compound is likely to be mainly (II*a*) or (II*b*), and the disaligenin compound (III). It was very significant from the point of view of successful resin formation, however, that the monosaligenin compound from 1-methyl-cyclohexene was accompanied by a small amount of a disaligenin compound, $C_{21}H_{24}O_2$. This contained one atom of active hydrogen per molecule, and apparently represented the simplest possible example of the linking of a polycondensed phenol-formaldehyde chain, *i.e.*, a Novolak, to the olefin[5]. This compound is formulated in (IV), the point of attachment of the hydrobenzyl group to the aromatic nucleus of the chroman unit being presumably *o*- or *p*- to the chroman oxygen.

When purified rubber (1 mole) in benzene was heated with saligenin in two different proportions (0.18 and 0.27 mole), two distinct oxygenated products were formed. These proved to contain hydroxylic (presumably phenolic) as well as ethereal oxygen, in the ratios 1 : 2 and 5 : 8, indicating that most of the oxygen was present in simple chroman units such as those in (III), and that roughly one chroman unit per 14 or per 8 isoprene units of the rubber was present. Not more than 1 in 2 or 5 in 8, respectively, of the chroman units could thus be carrying a hydroxybenzyl substituent or, if still larger phenol-formaldehyde substituents than hydroxybenzyl were present, then the proportion of chroman units carrying side chains (of any kind) would be smaller still. Confirmation of the constitutions advanced above has been sought by spectrographic means.

Absorption spectra.—Webb and others[6] gave data for the light absorption in hexane solution of a number of alkyl-substituted phenols, chromans, and coumarans, all of which exhibit a group of two or more narrow bands in the region 2700–2900 A.U. They found that the formation of chroman or coumaran rings by cyclization of *o*-alkylphenols is regularly associated with a well-marked increase and bathochromic shift of absorption, and that the exact location and intensity interrelationships of the fine structure bands is also highly characteristic of any given compound. We have, therefore, determined the ultra-violet absorption spectra (in cyclohexane solution) of saligenin and its various condensation products for purposes of identification.

Saligenin itself (Figure 1, curve *a*) gives rise to two bands near 2730 and 2800 A.U., closely similar to the spectra of *o*-cresol[7] and *o*-allylphenol[6] which only differ in the nature of the *o*-alkyl substituent. This absorption is intensified and displaced towards longer wave-lengths on passing to the compound of saligenin with methylcyclohexene (I*a*) (cf. Figure 1, curve *b*), which is characterized by two steep maxima situated at precisely the same wave-lengths as the two bands of 2,2-dimethylchroman[6] (2775 and 2845 A.U.; minimum at 2815 A.U.). The width and relative height of the bands are also the same for both compounds, although all our intensities are consistently higher than Webb's on the absolute molecular scale ($\epsilon = 3100$ at 2845 A.U.). The new compound evidently contains the same chromophoric grouping as 2,2-dimethylchroman, and its formulation as a methyl-substituted hexahydroxanthen (I*a*) may be considered as established beyond any doubt.

Again, the two substances $C_{17}H_{24}O$ and $C_{24}H_{30}O$, obtained by condensation of saligenin with dihydromyrcene, at one and at both (respectively) of the double bonds of the latter, exhibit absorption curves identical with the above. The molecular extinction coefficients at 2845 A.U. are now 3000 and 5650,

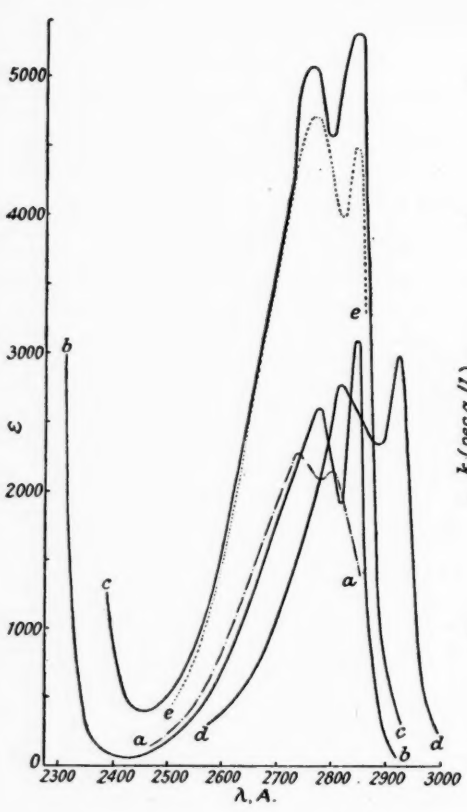


FIG. 1

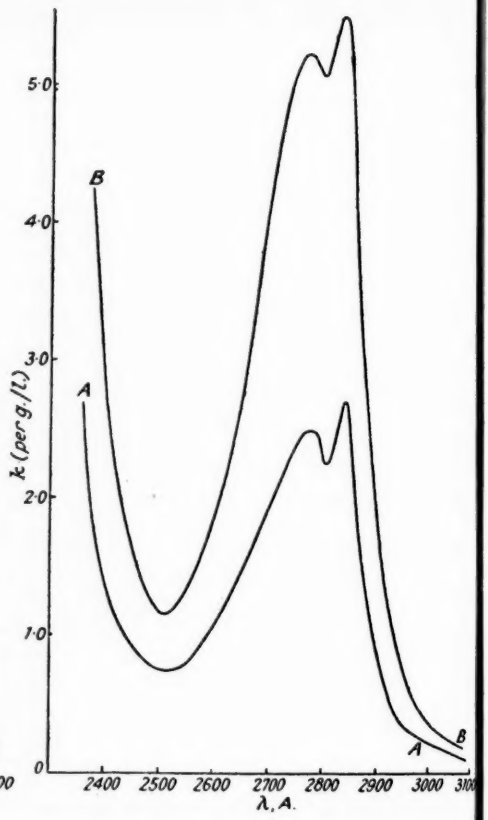


FIG. 2

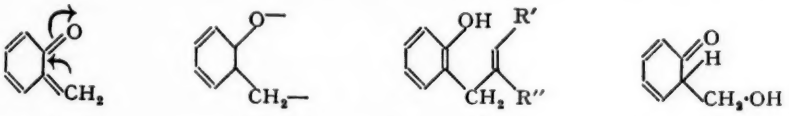
respectively, in good agreement with the proposed structures (II, *a* or *b*) and (III) which contain the 2,2-dialkylated chroman chromophore once or twice in the dihydromyrcene chain. Although the spectra of (II*a*) and (II*b*) would be indistinguishable, it seems likely that all our chroman derivatives must carry the extra methyl groups derived from the olefin in the 2-, and not the 3-position to produce complete identity with the spectrum of Webb's prototype.

Curve *c* of Figure 1 shows the extinction values of the solid hydroxybenzyl-substituted chroman derivative (IV). Its total absorption must be expected to bear close resemblance to the sum of the separate absorptions contributed by the *o*-hydroxybenzyl and the (nuclear-substituted) chroman chromophores which are effectively isolated from one another in the compound molecule[8]. This sum is graphically represented by the dotted curve *e*, except in the important respect that no allowance is made for the effect of nuclear substitution on the spectrum of the chroman system shown in curve *b*. We have been able to test that effect directly as regards the *p*-position by synthesizing the *p*-methyl derivative (V) (curve *d*). The general appearance of the spectrum remains unchanged, but a significant displacement of the maxima to 2815 and 2920 A.U. is observed. Since it is known that such bathochromic shifts are largely independent of the precise nature of the alkyl substituent (methyl, ethyl, and

benzyl groups all displace the absorption of benzene to longer wave-lengths[9]), it must be concluded that the hydroxybenzyl derivative (IV), in giving rise to a spectrum that terminates very abruptly beyond 2845 A.U., cannot contain the substituent affixed in the *p*-position. On the other hand, the difference between the observed and the constructed curve, *c* and *e*, can be well accounted for by formulating the hydroxybenzylchroman with the hydroxybenzyl group attached at the *o*-carbon atom. Both phenol and *o*-cresol (but not *p*-cresol) exhibit maximum absorption at the same wave-lengths[10], and the near-ultraviolet band of 2-methylcoumaran is considerably intensified but not displaced as the result of *omm'*-trisubstitution[6]. It has, indeed, been stated as a general rule for aromatic compounds that *o*-substitution produces only slight, and *p*-substitution relatively marked, bathochromic effects[11].

Finally, the absorption spectra of the two rubber-saligenin compounds (containing 2.25 per cent and 4.15 per cent of total oxygen, respectively) were measured in solutions of cyclohexane containing 10 per cent of ethyl alcohol. This choice of solvent was governed by the difficulty of obtaining optically clear solutions, but it was found that none of the curves of Figure 1 was appreciably altered by addition of the alcohol. Purified rubber itself does not exhibit selective absorption in the quartz ultraviolet, and the typical steep maxima at 2845 and near 2775 A.U. of the curves *A* and *B* (Figure 2) obtained for the two rubber derivatives must clearly be attributed to the presence of the chroman chromophore attached to the rubber chain. Allowance being made for increased general absorption, and a 5 : 8 ratio of phenolic to ethereal oxygen (see above) being assumed, the maximum specific extinction coefficient of curve *B* indicates that an average number of one in every ten isoprene units has reacted with a saligenin or *o*-substituted saligenin group. This figure is lower than the value of one in eight obtained from the total oxygen content, but certainly serves to show that the bulk of the saligenin must be attached to the rubber molecule by way of the chroman linkage.

Mechanism and course of reaction.—The precise mechanism by which the reactive groups of saligenin or other *o*-hydroxybenzyl alcohols unite with olefinic centers is not easy to determine. It might be supposed that the phenolic alcohol loses water internally to give momentarily either a strongly polarized form (*a*) or a resonating radical form (*b*), or else condenses directly with the olefin to give (*c*) as intermediate. The last course is not a likely one for non-benzenoid primary alcohols to pursue, and the lability of the hydroxyl group must arise from the nearness of the phenolic nucleus. This being so, probably the keto-form (*d*) of the phenolic alcohol is responsible for the reaction, under-



(*a*) (*b*) (*c*) (*d*)

going internal dehydration to give the vinyl ketone (*a*). If combination of this ketone with the olefin occurred in Diels-Alder fashion[12] to some extent through the form (*b*) and not wholly ionically through (*a*), the final condensation products would be likely to contain many isomeric forms, *e.g.*, I*b* as well as I*a*. The spectrographic evidence, however, does not point to the existence of the additional forms which would arise by two-direction addition of olefin to ketone.

As regards the conclusion that attachment of the hydroxybenzyl side chain in (IV) is restricted to the *o*-position in the chroman system (and this appears to apply also to the points of junction of the side chains in the rubber derivatives), it should be pointed out that the restriction may well not hold between phenol-formaldehyde units throughout the longer Novolak chains which would normally be formed where higher proportions of phenol and formaldehyde to olefin and an acid condensing catalyst were used. Also, it is quite likely that when maleic anhydride is used as the acid catalyst some or all of it ultimately combines with the phenol-formaldehyde condensation products, since Hultzsch[4] found that ethyl maleate combines readily with these. The superior ease of combination of highly oxidized rubber over rubber hydrocarbon appears to be solely a function of miscibility of the reactants. The greatly shortened, oxygenated chains of the highly oxidized rubber (*M*, 3000–4000) dissolve fairly readily in boiling phenol, whereas rubber is insoluble.

The rubber-linked Novolaks formed in presence of an acid catalyst are capable of being cross-linked to yield three-dimensional molecular networks of the Bakelite type when heated in the ordinary way with hexamethylenetetramine. The resulting thermosetting products, however, soften when they are heated to 120–130° and harden again when they are cooled.

EXPERIMENTAL

1-*Methylcyclohexene.*—The hydrocarbon, b. p. 110°, was obtained by dehydration of 1-methylcyclohexanol in the presence of a little iodine (found: C, 87.45; H, 12.65; I.V., 265; calc. for C_7H_{12}: C, 87.5; H, 12.5%; I.V., 265).

o-Hydroxybenzyl alcohol.—Commercial saligenin, crystallized twice from ethyl alcohol-benzene (15 : 85 by vol.) formed colorless plates, m. p. 86° (found: C, 67.85; H, 6.5; calc. for $C_7H_8O_2$: C, 67.7; H, 6.44%).

12-*Methyl*-1,2,3,4,12,13-*hexahydroxanthen* (Ia).—Saligenin (40 g.) was heated with excess of 1-methylcyclohexene (200 cc.) for 4 hours at 180° in sealed tubes. The tubes, on cooling, contained a pale yellow solution and a little water; the latter was removed with anhydrous copper sulfate. After the excess of olefin had been removed by distillation at reduced pressure a syrup (54 g.) remained. This syrup was dissolved in benzene (500 cc.), washed twenty times with aqueous 2 *N* caustic potash (4 l.), and finally with water until neutral. The benzene solution was dried, and the solvent removed by distillation, leaving a pale yellow, mobile oil (43 g.). Fractional distillation of this oil, through a Fenske column, furnished 12-*methyl*-1,2,3,4,12,13-*hexahydroxanthen* (30 g.), a colorless, nonsolidifying, mobile oil, b. p. 138–139°/10 mm. (found: C, 83.15; H, 9.0; $C_{14}H_{18}O$ requires C, 83.17; H, 8.9%). A brown thermoplastic residue (13.0 g.) remained.

The oily condensation product did not possess ketonic or aldehydic properties, and was not hydrolyzable. A sample of it did not absorb hydrogen when shaken for 6 hours with the gas in presence of Adams's catalyst; a similar sample failed to liberate methane when treated with methylmagnesium iodide according to Bolland's modification of the Zerewitinov method. The condensation product, therefore, was an ether, without nonbenzenoid unsaturation or hydroxyl groups.

5-*o-Hydroxybenzyl*-12-*methyl*-1,2,3,4,12,13-*hexahydroxanthen* (IV).—The undistillable thermoplastic residue (2 g.) was purified by dissolving it in benzene-petroleum (1 : 1 by vol.; 300 cc.), running the solution through a column of alumina, and well washing the adsorbate with the same solvent (2 l.). The

filtrate gave on evaporation the compound (IV) (1.2 g.), in which the *o*-hydroxybenzyl group, as shown by spectrographic examination, occupied the 5-position. This was an amorphous resinous solid (found: C, 81.8; H, 8.0; OH, 5.3; $C_{21}H_{24}O_2$ require C, 81.8; H, 7.8; OH, 5.5%).

Dihydromyrcene.—Myrcene, prepared from bay oil (*Pimenta acris*) by the method of Power and Kleber[13], was reduced with sodium and alcohol as described by Semmler and Mayer[14]. The hydrocarbon, after being twice distilled over sodium through a Fenske column, boiled at 58–59°/16 mm. (found: C, 87.05; H, 13.0; I.V., 364; calc. for $C_{10}H_{18}$: C, 86.9; H, 13.1%; I.V., 368).

Monosaligenino-dihydromyrcene.—Saligenin (24 g.) was heated with dihydromyrcene (120 cc.) for 2 hours at 180° in a sealed tube. The condensate was isolated in the usual manner and the yellow oil (32.6 g.) so obtained was fractionally distilled. *Monosaligenino-dihydromyrcene* (20.2 g.), b. p. 118°/0.05 mm., probably consisting mainly of *2,2-dimethyl-3-(γ-methyl-Δγ-pentenyl)-chroman* (IIa), was first obtained (found: C, 83.4; H, 9.9; $C_{17}H_{24}O$ requires C, 83.5; H, 9.85%). Further distillation gave nearly pure *disaligenino-dihydromyrcene* (5.4 g.), a viscous brown syrup, b. p. 200–205°/0.05 mm. Purification of the latter by adsorbing it on alumina from solution in petroleum, followed by elution of the adsorbate with benzene-petroleum (1 : 1 by vol.), gave an almost colorless syrup, doubtless *α-(2,2-dimethylchromanyl-3)-β-(2,3-dimethylchromanyl-2)-ethane* (III) (found: C, 82.3; H, 8.7; $C_{24}H_{30}O$ requires C, 82.3; H, 8.6%). The monosaligenino-compound (0.2659 g.), in ethanol solution, absorbed hydrogen (24.8 cc. at N.T.P.) equivalent to one double bond per molecule when shaken for 6 hours with Adams's catalyst (0.1 g.). The disaligenino compound under the same conditions did not absorb hydrogen. Neither derivative gave any methane with methyl-magnesium iodide under Bolland's modified conditions of Zerewitinov hydroxyl determination, and neither showed ketonic or aldehydic properties or was hydrolyzable.

Rubber.—For convenience, a "sol" fraction of rubber, obtained by partial dissolution of crepe rubber in light petroleum (b. p. 40–60°), was employed. The crepe rubber was cut up and thoroughly extracted with acetone in the usual manner, and the residue then extracted with light petroleum in the all-glass modification of Pummerer, Andriessen, and Gündel's apparatus described by Bloomfield and Farmer[15]. In the latter operation the extracts obtained in the first 48 hours were rejected as containing oxygenated rubber, and the later extracts were well mixed and their rubber content precipitated by addition of excess of 95 per cent alcohol. The solvent and alcohol adhering to the rubber were removed by evaporation at 10 mm. pressure, and the rubber finally dried for 48 hours at room temperature and 10^{-5} mm. pressure. The rubber so obtained was kept under a high vacuum in the dark (found: C, 88.05; H, 11.95; I.V., 371; *M*, 361,000; calc. for C_5H_8: C, 88.2; H, 11.8%; I.V., 372).

Saligenino rubber.—Rubber (1.0 g.) was dissolved in toluene (25 cc.) and heated with saligenin (0.33 g.) in a sealed tube containing oxygen-free nitrogen for 4 hours at 180°. After cooling, the tube contained a pale yellow solution and some water. Benzene (150 cc.) was added, and the solution dried over anhydrous sodium sulfate, filtered, and concentrated under nitrogen at reduced pressure to 35 cc. The clear solution so obtained was poured into an excess of ethyl alcohol, which precipitated the saligenino-rubber as a white rubberlike solid, leaving the self-condensation products of saligenin in solution. The precipitate was washed once with ethyl alcohol and thoroughly dried for 48 hours at 10^{-5} mm. by distillation of all solvent into a liquid-air trap (found: C, 86.5; H, 11.25; OH, 0.8%; *M*, 119,000). Assuming that all the non-

hydroxylic oxygen is ethereal, we calculated that one chroman linkage was present per 14 isoprene units (cf. the value found spectroscopically). A second saligenino rubber, a white rubberlike solid, was prepared by heating rubber (1.8 g.) in toluene with a larger proportion of saligenin (0.9 g.) than was used in the foregoing experiment (found: C, 85.3; H, 10.55; OH, 1.8%; *M*, 69,000). In this derivative, one chroman linkage was present per eight isoprene units as calculated from the above analytical data.

7,12-*Dimethyl*-1,2,3,4,12,13-*hexahydroxanthen* (V).—2-Hydroxy-5-methylbenzyl alcohol, m. p. 105° (3 g.), was heated with 1-methylcyclohexene (15 cc.) for 3 hours at 180° in a sealed tube. The pale yellow liquid product was freed from water by drying over anhydrous sodium sulfate, and then from solvent. The syrupy residue (3.8 g.) was dissolved in "AnalaR" benzene, and the solution washed twenty times with 2 *N* aqueous potassium hydroxide. The solvent was then removed, and the residue (3.3 g.) fractionally distilled. The first fraction had b. p. 147–150°/10 mm. (found: C, 82.95; H, 9.4; $C_{15}H_{20}O$ requires C, 83.25; H, 9.3%), and the nonhomogeneous residue consisted of substances of somewhat higher oxygen content.

Spectrographic measurements.—The spectra were recorded on Kodak B-10 plates, using a Spekker photometer and Hilger small spectrograph, which gives a dispersion of 35 A.U. per mm. in the region of 2800 A.U. Cyclohexane and ethyl alcohol were both purified for spectroscopic use.

ACKNOWLEDGMENT

We thank W. T. Chambers and (Miss) H. Rhodes for carrying out the microanalyses in this work, which forms part of the program of fundamental research on rubber undertaken by the Board of the British Rubber Producers' Research Association.

REFERENCES

[1] Bacon and Farmer, *Proc. Rubber Tech. Conf. London*, **1938**, 256.
[2] Redfarn and Schidrowitz, British patent 507,995.
[3] Hilditch and Smith, *J. Soc. Chem. Ind.* **54**, 111 (1935).
[4] Hultzsch, *J. prakt. Chem.* **158**, 275 (1941).
[5] No long Novolak chains were to be expected, since an excess of olefin was always used.
[6] Webb, Smith, Bastedo, Ungnade, Prichard, Hoehn, Wawzonek, Opie and Austin, *J. Org. Chem.* **4**, 389 (1939).
[7] Hogness, Sidwell and Zscheile, *J. Biol. Chem.* **120**, 251 (1937).
[8] Jones, *Chem. Rev.* **32**, 2 (1943).
[9] Ley and Dirking, *Ber.* **67**, 1333 (1934).
[10] Wolf and Herold, *Z. physik. Chem.* [B] **13**, 229 (1931).
[11] Morton and Stubbs, *J. Chem. Soc.*, **1940**, 1347.
[12] Compare the dimerization of methylvinyl ketone, Alder, Offermans and Rüden, *Ber.* **74B**, 905, 906 (1941).
[13] Power and Kleber, *Pharm. Rundschau* **13**, 60 (1895).
[14] Semmler and Mayer, *Ber.* **44**, 2010 (1911).
[15] Bloomfield and Farmer, *Trans. Inst. Rubber Ind.* **16**, 69 (1940).

THE COURSE OF AUTOÖXIDATION REACTIONS IN POLYISOPRENES AND ALLIED COMPOUNDS

VII. REARRANGEMENT OF DOUBLE BONDS DURING AUTOÖXIDATION *

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In Part V of this series[1], it was reported that a typical drying-oil ester, methyl docosahexaenoate, showed a marked increase in its capacity to absorb ultraviolet light as the result of exposure to atmospheric oxygen in the illumination of the laboratory. The rapid peroxidation of the polyene system which set in during this exposure promoted a structural change apparently of a conjugative nature. The nature of this change is now examined. Two types of unconjugated unsaturation are, however, taken into consideration: (1) the methylene-interrupted unsaturation, $\cdot C{:}C\cdot C\cdot C{:}C\cdot C\cdot C{:}C\cdot$, characteristic of numerous unconjugated drying-oil acids such as linoleic, linolenic, and various polyene fish-oil acids, and (2) the more widely spaced unsaturation found in rubber and in other unconjugated polyisoprene hydrocarbons. The structural changes that ensue on oxidation are of particular interest in relation to the free-radical mechanism of olefinic peroxidation already formulated by Farmer, Bloomfield, Sundralingam, and Sutton[2], in which the olefin is regarded as passing through the stages:

$$\cdot CH\cdot C{:}C\cdot \rightarrow \cdot \underset{*}{C}\cdot C{:}C\cdot \rightarrow \cdot \underset{OO^*}{C}\cdot C{:}C\cdot \rightarrow \cdot \underset{OOH}{C}\cdot C{:}C\cdot$$

the asterisk representing the radical center.

Materials.—For the purpose of differentiating clearly the effect of oxidation from that of (1) thermal treatment[3] and (2) alkali treatment[4], it has been necessary to work with substances as nearly as possible spectroscopically pure. For this reason subjection of the substances during their preparation to temperatures above 115°, to prolonged treatment with alkali, or to the action of atmospheric oxygen was highly undesirable. Ethyl linolenate represented a favorable case for study, the only undesirable feature attending its preparation being the necessity to subject the parent linseed oil to a short saponification with alkali. Methyl docosahexaenoate, which was selected to represent the unconjugated polyene esters derived from fish oils, had also to be submitted to short treatment with alkali at the first stage of its preparation, but the use of high temperatures, and exposure to oxygen during its laborious isolation were altogether avoided by a modification of Farmer and Van den Heuvel's original method[5]. The yellow color of the fish-oil ester, which developed rapidly in the presence of oxygen, could only be completely removed by

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chromatographic treatment of the ester with alumina in an atmosphere of purified nitrogen. Squalene and rubber were employed to exemplify the second type of unsaturation. The former was rectified by molecular distillation below 112°, and then further purified by chromatographic treatment in purified nitrogen, and the latter was freed almost entirely from impurities by fractional dissolution of crepe rubber in petroleum-acetone in an atmosphere of nitrogen.[6]

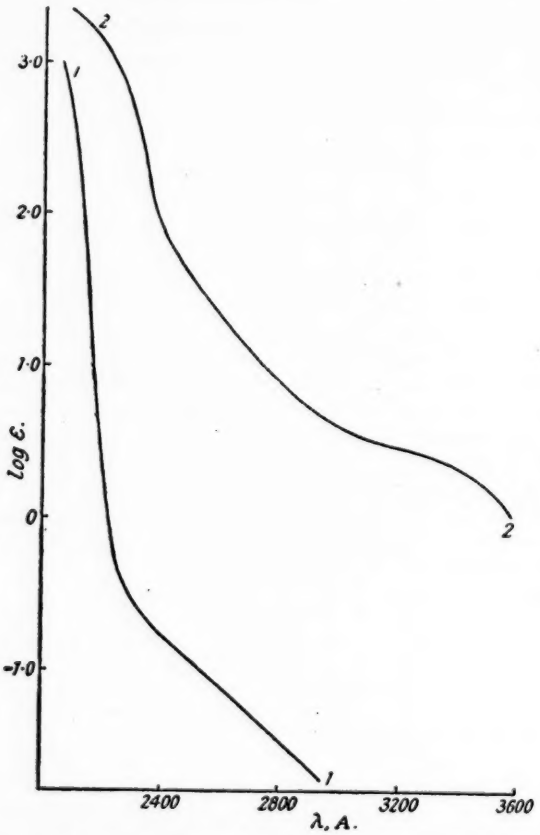


FIG. 1.—Spectra of cyclohexene (1) and cyclohexene hydroperoxide (2) in cyclohexane.

Spectrographic examination of autoöxidized substances.—In determining the structural cause of the strong light-absorbing capacity of the autoöxidized fish-oil ester, it was necessary at the outset to gain information concerning the peroxide chromophore. This has been examined in detail, and it is found that the strong light-absorption in the regions of 2400 and 2700 A.U. is not to be attributed to the peroxido-olefin structure, but must be associated with the formation of conjugated groups by double-bond shift in the carbon chain during its oxygenation. The spectrum of a typical olefin peroxide is compared with that of the parent olefin in Figure 1. The most interesting features are the widely increased general absorption and the new broad band beyond 3000 A.U., but the extinction values are low throughout the ultraviolet range.

Simple alkyl peroxides appear to be even more transparent[7], so the influence of peroxidic absorption can certainly be neglected in the presence of typical organic chromophores.

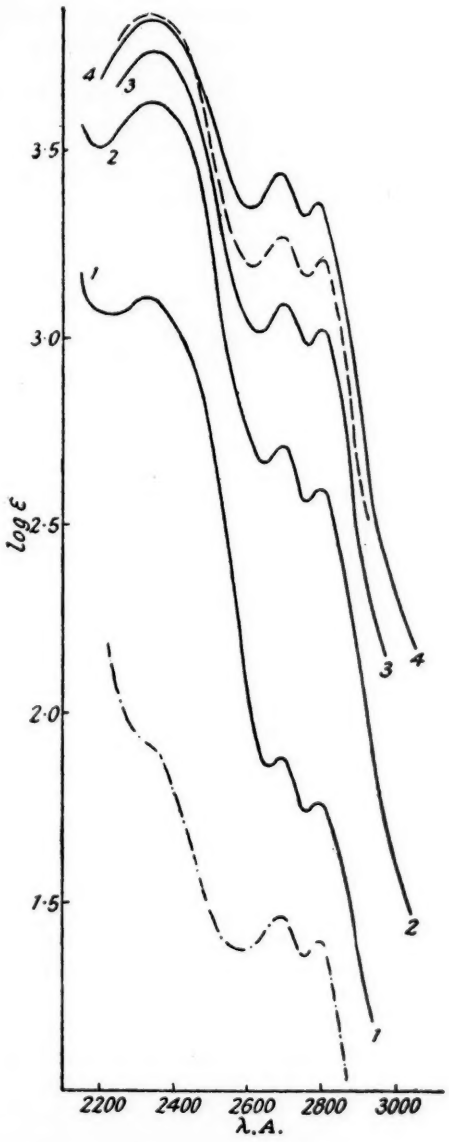


FIG. 2.—Spectra of ethyl linolenate (in ethanol)—

—·—·—·— Before oxidation.
——— After 1.2% (1), 3.9% (2), 6.5% (3), and 11% (4) oxidation.
- - - - - After 8.5% oxidation in darkness.

Spectrographic analysis of the early stages of atmospheric oxidation of ethyl linolenate,

$$CHEt:CH\cdot CH_2\cdot CH:CH\cdot CH_2\cdot CH:CH\cdot [CH_2]_7\cdot CO_2Et,$$

during which all the incorporated oxygen survives in peroxidic form, has revealed the emergence of intense selective absorption in two well-defined wavelength regions (cf. Figure 2). In the absence of any possible chromophoric oxygen groups, maximum absorption near 2340 A.U. is known to characterize the spectrum of a straight-chain conjugated diene[8], and the two narrow bands at 2690 and 2800 A.U. are typical of straight-chain conjugated trienes such as elæostearic acid or alkali-isomerized linolenic acid[9]. The starting material (dotted curve, Figure 2) evidently contains traces of similar absorbing compounds as impurities.

Assuming maximum molecular extinction coefficients of 24,400 and 47,300 for ethyl-alcoholic solutions of pure conjugated diene and triene, respectively[10],

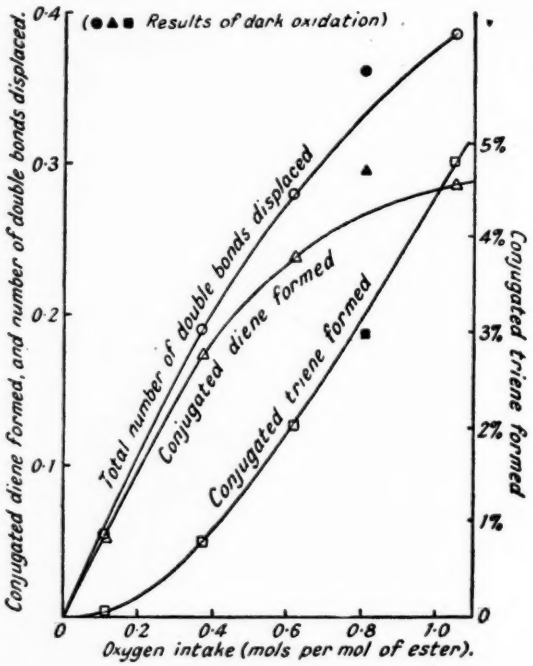


FIG. 3

and allowing for irrelevant absorption at 2690 A.U. due to the ascending branch of the short-wave band at 2340 A.U., we can estimate the actual amounts of conjugated material produced from ethyl linolenate during autoöxidation. In Figure 3 the number of conjugated diene groups per mole of ester and the percentage concentration of conjugated triene formed are plotted against the observed intake of oxygen. It can be seen that, after the incorporation of 1 mole of oxygen, rearrangement of double bonds has progressed to a stage at which approximately 28.5 per cent of the ester taken contains two double bonds

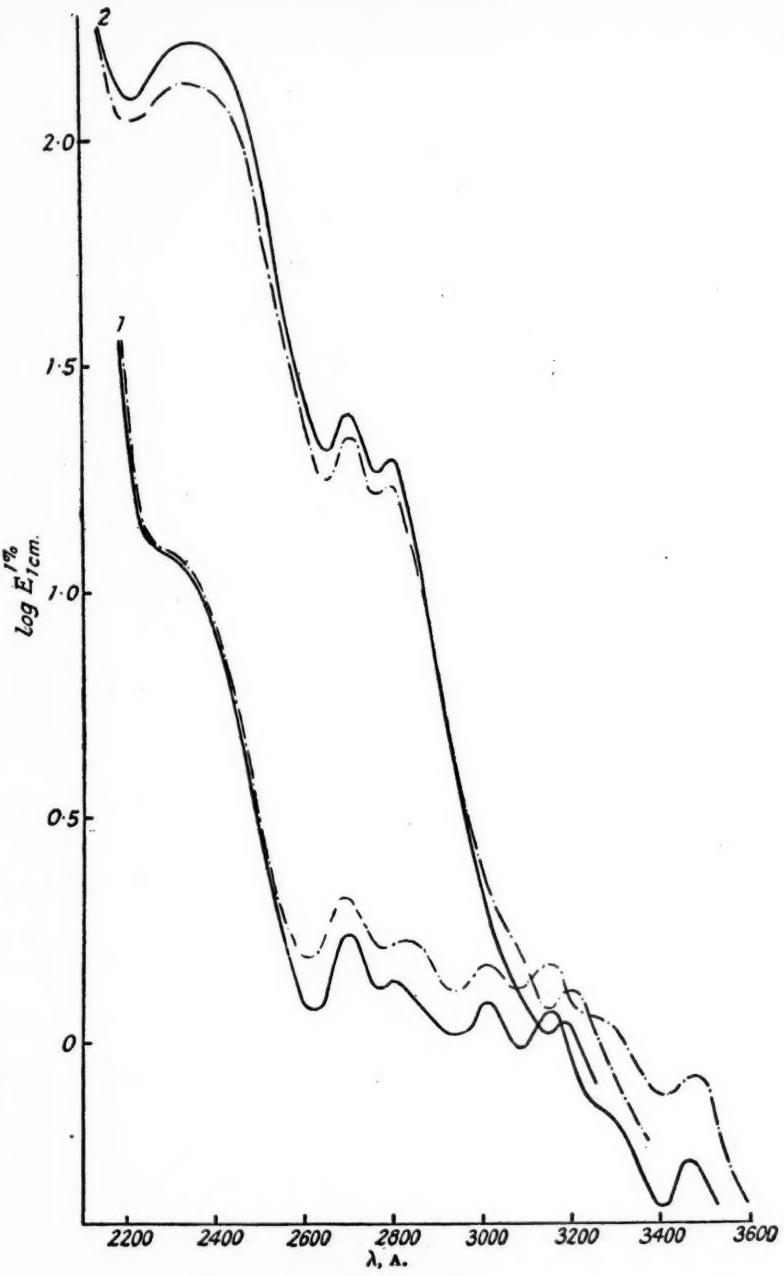


FIG. 4.—Spectra of methyl docosahexaenoate (in ethanol).

—·—·—·— Sample a before and after 6% oxidation.
——— Sample b before and after 7% oxidation.

in conjugation, and 4.5 per cent has all three double bonds conjugated. The top curve of Figure 3 represents the total number of double bonds displaced, account being taken of the fact that two double bonds must be shifted for each conjugated triene system formed. The initial slope of this curve shows that during the early stages of autoöxidation each molecule of oxygen absorbed is 50 per cent effective in moving one double bond into conjugation.

The absorption spectra of two samples of methyl docosahexaenoate were also examined before and after autoöxidation, and the occurrence of the same process of double-bond rearrangement during oxidation is revealed by the development of intense absorption in the originally feebly absorbing regions of

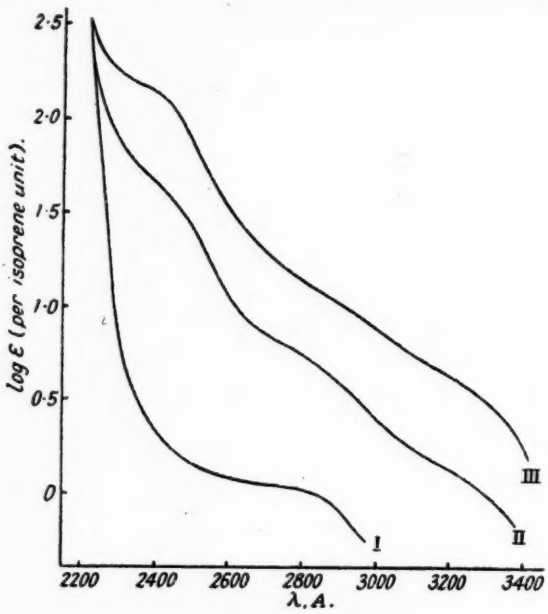


FIG. 5.—Spectra of squalene (in cyclohexane).
I, Chromatographically purified squalene.
II, Chromatographically after 3.7% U.V. oxidation.
III, Chromatographically after 9% U.V. oxidation.

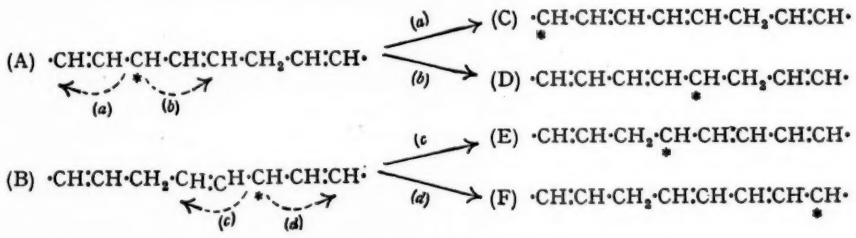
2340 and 2700 A.U. (Figure 4). The bands near 3015, 3165, 3290, and 3480 A.U. exhibited by the unoxidized ester were also observed by Edisbury, Morton, and Lovern[11] in all their samples of fish-oil acids, and are doubtless due to the presence of traces of higher conjugated polyenes. An important effect of autoöxidation is the destruction of these conjugated systems implied by the decreased absorption at longer wave-lengths. The new band at 3190 A.U. is probably associated with the triene spectrum[12].

The rearrangement phenomenon was overlooked by Treibs[13], who studied the course of autoöxidation of linoleic, linolenic, and liver-oil hexaene esters refractometrically; he found that there is no exaltation of the molecular refraction which could be ascribed to conjugated unsaturation after the incorporation of 1 mole of oxygen. This finding agrees with our own observations on autoöxidized methyl docosahexaenoate[1], but in our experience the original ester

always showed an exaltation of approximately 1 unit, which disappeared as autoöxidation (accompanied by rapid increase in the density and comparatively slow increase in the refractive index) proceeded[14]. Refractivity measurements are clearly unreliable as a guide to the presence of conjugation in the highly autoöxidizable substances displaying methylene-interrupted unsaturation.

In contrast to the foregoing, when solutions of carefully purified squalene and of fractionated rubber were similarly examined before and after autoöxidation, no strong increase in the absorption of light which could definitely be ascribed to the formation of conjugated units was observed. The spectra for squalene and two of its oxidation products (3.7% and 9% oxygen-intake) are represented in Figure 5. The small increases in absorption there shown may be due to small degrees of conjugation, or to the formation of peroxide groups (cf. the effect on light absorption of peroxide groups in the case of cyclohexene), or to a combination of both.

Course of conjugative change.—If the first stage of peroxidation consists in the severance (presumably by the aid of molecular oxygen) of a thermally or photochemically activated α-methylenic C—H bond, so leaving an olefinic free radical, it may be expected that resonance between the two 3-carbon forms $\cdot\overset{3}{C}H:\overset{2}{C}H\cdot\overset{1}{C}H\cdot$ and $\cdot\overset{3}{C}H\cdot\overset{2}{C}H:\overset{1}{C}H\cdot$ will immediately follow, so that when in succession a molecule of oxygen and an atom of hydrogen (the latter probably detached from a nearby molecule) come to be incorporated, there is an approximately equal tendency for the ·OOH group to appear at the positions 1 and 3, and for the double bond to remain at the original position or to appear at the adjacent C—C bond. In the methylene-interrupted type of unsaturation considered above, the most reactive methylene groups are those flanked on either side by a double bond, and if the two methylene groups of this type in ethyl linolenate were to be attacked singly by oxygen the original radical forms (A) and (B) would be supplemented by (C)—(F):



The hydroperoxides derived from (C)—(F) would then show diene conjugation. Similarly if both the reactive methylene groups were attacked consecutively by oxygen, which would happen frequently only in advanced stages of oxidation, then five other (di-)peroxido forms would become possible, three of which would show diene conjugation, one triene conjugation, and the last the original state of unconjugation. Now if on each occasion that a hydrogen atom is detached from just one of the active methylene groups of a linolenic molecule the tendency for the radical center so formed to migrate to left or right is assumed to be about equal to the tendency for it to retain its original position, it follows that only half the radical molecules that are ultimately successful in combining with oxygen and hydrogen to give monohydroperoxido compounds

yield conjugated forms; if, however, all of the three resonance forms derivable by loss of a hydrogen atom from a pentadiene system $\cdot CH:CH\cdot CH_2\cdot CH:CH\cdot$ are to be regarded as possessing equal stability, the proportion of conjugated to unconjugated forms will rise to about 2 : 1. Since the hydroperoxido derivatives of ethyl linolenate undergo little decomposition during the absorption of the first molecule of oxygen by the ester, the quantitative relationship between the conjugated and the unconjugated forms produced is likely to have remained substantially unchanged by secondary reaction in the present experiments: the product, however, at the end of the "monoperoxidation" stage is likely to have contained diperoxido and unchanged ester molecules as well as monoperoxido derivatives.

In the case of the polyisoprene hydrocarbons, however, the reactive α-methylene groups are flanked only on one side by double bonds. This leads in practice to a much lower reactivity of the olefin, and, in terms of the hypothesis, to the necessity for two successful peroxidations to occur in any unconjugated diene unit of the chain (C:C·C·C·C:C) before diene conjugation can appear therein. Furthermore, the hydroperoxide groups formed in these compounds are very unstable, so that no very high (overall) percentage of peroxidic oxygen survives at the end of an experiment, and this applies whether the oxidation is restricted to an early stage or whether it is carried (in ultraviolet light) to an advanced stage; also the decomposition of the peroxide groups leads to a corresponding degree of destruction of unsaturation. It is not surprising therefore that, in practice, peroxidation does not produce any considerable degree of conjugation. The occurrence, however, of peroxidation at all in rubber, squalene, etc., may well cause change in the original arrangement of the double bonds, and so contribute to the observed heterogeneity of the final oxidation products, *e.g.*:

$$\cdot CMe:CH\cdot CH_2\cdot CH_2\cdot CMe:CH\cdot \rightarrow \cdot CMe:CH\cdot CH_2\cdot CH:CMe\cdot CH(OOH)\cdot$$

or

$$\cdot CMe(OOH)\cdot CH:CH\cdot CH_2\cdot CMe:CH.$$

Presumably the easily oxidizable forms displaying methylene-interrupted unsaturation which ought thus to be produced by the first double-bond shift do not accumulate sufficiently in the earlier stages of autoöxidation to cause by their further oxidation appreciable change in the direction of conjugation over the whole material; also in the more advanced stages where their numbers should increase their effect is nullified by the destruction of unsaturation accompanying peroxide decay.

If the free-radical mechanism of autoöxidation is the correct one, double-bond shifts appear not unlikely to occur also in the autoöxidation of monoölefinic substances, since the 3-carbon grouping $\cdot CH:CH\cdot CH\cdot$ is concerned here also, so that methyl oleate should give the peroxido forms $\cdot C_{11}:C_{10}\cdot C_9(OOH)\cdot C_8$ and $\cdot C_{11}\cdot C_{10}(OOH)\cdot C_9:C_8\cdot$ as well as $\cdot C_{11}(OOH)\cdot\cdot C_{10}:C_9\cdot C_8\cdot$ and $\cdot C_{11}\cdot C_{10}:C_9\cdot C_8(OOH)$. This deduction has not been tested experimentally, but the fully hydrogenated derivatives of hydroperoxidoöleic acid which were described in Part IV[15] may well include 9- and 10-, as well as 8- and 12-hydroxystearic acid. In addition, since the production of conjugated forms from the above-mentioned substances has never been observed to occur in the entire absence of oxygen, even after many hours of illumination in ultraviolet light, the further deduction can hardly be resisted that molecular

oxygen (in spite of various recorded observations to the effect that the rate of autoöxidative reaction in olefins is independent of the oxygen concentration) plays a direct part in detaching sufficient hydrogen atoms[16] from the α-methylenic C—H bonds to initiate the necessary reaction chains for bringing about successful autoöxidation.

No distinction has hitherto been made in this series between the course of photochemical and that of thermal oxidation, since not only have experimental conditions in which both thermal and photochemical activation are possible usually been employed, but no results pointing to the functioning of two different mechanisms of oxygen incorporation have yet been obtained. It is now found that, apart from the induction period (see below), the result of conducting an oxidation of ethyl linolenate at room temperature in complete darkness is exactly the same with regard to efficiency of peroxide formation and the extent of double bond rearrangement as that obtained in (summer) daylight. The dotted curve in Figure 2 represents the absorption spectrum of this thermally oxidized ethyl linolenate (8.5 per cent oxygen uptake), and the three black points in Figure 3 the extent of conjugation and the total double-bond shift produced by the oxidation. The free-radical mechanism of peroxidation, therefore, appears to apply to thermal as well as to photoöxidation. It is of interest also that the analogy formerly pointed out by one of us[17] between the mechanism of olefinic autoöxidation and that of maleic anhydride addition to olefins at high temperatures clearly needs to be extended to include double-bond shifts in the latter reaction exactly comparable with those reported above to occur in the former. Alder[18] has recently observed that both maleic anhydride and azodicarboxylic esters unite with allylbenzene to give adducts of the type $CHPh:CH\cdot CH_2R$ (not $CHPhR\cdot CH:CH_2$), R representing the maleic or azodicarboxylic grouping, and similar results obtained by one of us will be published later.

EXPERIMENTAL

Cyclohexene.—Cyclohexene was purified for optical examination by the method of Stücklen, Thayer, and Willis[19], who record, over the range examined by them, an absorption curve identical with that given in Figure 1.

Cyclohexene peroxide.—This was prepared by Farmer and Sundralingam's method[20] and twice distilled at 27°/0.03 mm. for spectrographic examination. Further distillation of the sample caused no change in the absorption curve.

Ethyl linolenate.—Hexabromostearic acid (m. p. 185°) was debrominated according to Norris, Kass, and Burr[21], and the resultant crude ester molecularly distilled at 78° (found: C, 78.3; H, 11.3; I.V., 246; calculated for $C_{20}H_{34}O_2$: C, 78.4; H, 11.2%; I.V. for $|\overline{\overline{\overline{3}}}$ 249). The ester was kept sealed in a vacuum until required for use, and its absorption spectrum determined within 40 mins. of opening the tube.

Autoöxidation.—Since no water is eliminated during the early stages of oxygenation[22], the oxygen intake was determined by direct weighing against a tare. Small beakers (2 cm. diameter) containing about 200 mg. each of the ester were exposed during June to a dust-free atmosphere at 20° ± 3° near a window facing north. At intervals, successive samples were reweighed, made up to a known volume in ethyl alcohol, and immediately used for spectrographic and peroxide determination, the latter by the method of Bolland, Sundralingam, Sutton and Tristram[23]. The observations were completed within 2 hrs. of reweighing. It was found that 1.1% of oxygen (P.O.C.,

1.3%) was absorbed in 24 hrs., 3.7% (P.O.C., 4.1%) in 48 hrs., 6.3% (P.O.C., 6.7%) in 72 hrs., and 12.0% (P.O.C., 10.3%) in 110 hrs. In the dark, no oxygen was absorbed by the ester during the first 2 days, but 8.7% (P.O.C., 8.1%) was found to be absorbed after 7 days.

Methyl docosahexaenoate.—The glycerides of cod-liver oil of good quality were converted by the action of methanolic hydrogen chloride into the corresponding methyl esters. From the mixed esters a fraction judged to contain the whole of the C_{23}-ester fraction was separated by a series of molecular distillations at temperatures below 115°. This fraction, containing some saturated and possibly some monoölefinic esters in addition to the polyene esters, was rapidly saponified with a small excess of methanolic potassium hydroxide, and the potassium soaps converted *via* the free acid into the corresponding lithium soaps. By fractional crystallization of the latter from acetone, the (relatively soluble) lithium soap of the crude hexaene acid was segregated, and thereafter converted *via* the free acid into the corresponding methyl ester. This was finally fractionated by molecular distillation. All operations were conducted in an atmosphere of purified nitrogen or in high vacuum. Two samples were employed: (1) one fraction distilled at 91° which still contained traces of the C_{23}-ester ($|\overline{5}$), and (2) another at 110° which gave satisfactory analytical values for the C_{23} ester ($|\overline{6}$).

Autoöxidation.—The oxidation technique was essentially similar to that outlined above. Sample (1) absorbed 6.3% (P.O.C., 5.8%) of oxygen in 72 hrs.; sample (2) (under rather more favorable conditions) 7.2% (P.O.C., 6.9%) in 28 hrs.

Squalene.—Portions of the purified squalene (found: C, 87.85; H, 12.35; calculated for $C_{30}H_{50}$: C, 87.72; H, 12.28%) were shaken (without solvent) with oxygen in ultraviolet light at *ca.* 35° until (1) *ca.* 3.5% and (2) *ca.* 9% of oxygen had been absorbed. The two products had: (1) C, 84.5; H, 11.85; O (diff.), 3.65; P.O.C., 1.7%, and (2) C, 79.8; H, 11.25; O (diff.), 8.95; P.O.C., 3.54%.

Rubber.—A sample of purified rubber, dissolved in spectroscopically pure cyclohexane, was shaken with oxygen at *ca.* 35° in ultraviolet light until *ca.* 1% of oxygen had been absorbed. The product had: C, 87.2; H, 11.75; O (diff.), 1.05%.

Spectrographic measurements.—The Spekker photometer was used in conjunction with a tungsten-steel spark and a Hilger Small Spectrograph E 484, which gives a dispersion of 30 A.U. per mm. at 2700 A.U. and 20 A.U. per mm. at 2340 A.U. Spectral photographs exhibiting a high degree of contrast were obtained on Kodak B-10 plates. Two concentrations of ester solution normally sufficed to cover the entire range of the spectrum when two different cell lengths were used. Cyclohexane and ethyl alcohol were specially purified for absorption measurements[24].

ACKNOWLEDGMENT

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REFERENCES

[1] Farmer and Sutton, *J. Chem. Soc.*, **1943**, 119.
[2] Farmer, Bloomfield, Sundralingam and Sutton, *Trans. Inst. Rubber Faraday Soc.* **38**, 348 (1942).
[3] Consult a forthcoming paper.
[4] Farmer, *Trans. Faraday Soc.* **38**, 357 (1942).

[5] Farmer and van den Heuvel, *J. Soc. Chem. Ind.* **57**, 24 (1938).
[6] Bloomfield and Farmer, *Trans. Inst. Rubber Ind.* **16**, 69 (1940).
[7] Lederle and Rieche, *Ber.* **62**, 2573 (1929).
[8] See the spectrum of alkali-isomerized linoleic acid, according to Mitchell, Kraybill and Zscheile, *Ind. Eng. Chem., Anal. Ed.* **15**, 1 (1943).
[9] Van der Hulst, *Rev. trav. chim.* **54**, 639 (1935); Mitchell, Kraybill and Zscheile, *Ind. Eng. Chem., Anal. Ed.* **15**, 1 (1943).
[10] Values calculated from the data of Mitchell, Kraybill and Zscheile, *Ind. Eng. Chem., Anal. Ed.* **15**, 1 (1943).
[11] Edisburg, Morton and Lovern, *Biochem. J.* **29**, 899 (1935).
[12] Van der Hulst, *Rev. trav. chim.* **54**, 639 (1935).
[13] Treibs, *Ber.* **75**, 925 (1942).
[14] An earlier normal value of $[R_L]_D$ reported by Farmer and van den Heuvel (*J. Chem. Soc.*, **1938**, 429) was due to unsuspected oxidation of the distilled ester.
[15] Farmer and Sutton, *J. Chem. Soc.*, **1943**, 119.
[16] Probably in the form of HOO* radicals. Kinetic studies of the course of the reaction will be published later by the author's colleagues.
[17] Farmer, *Trans. Faraday Soc.* **38**, 340 (1942).
[18] Alder, *Ber.* **76**, 27 (1943).
[19] Stucklen, Thayer and Willis, *J. Am. Chem. Soc.* **62**, 1717 (1940).
[20] Farmer and Sundralingam, *J. Chem. Soc.*, **1942**, 132.
[21] Norris, Kass and Burr, *Oil and Soap* **17**, 123 (1940).
[22] Farmer and Sutton, *J. Chem. Soc.*, **1943**, 119; Treibs, *Ber.* **75**, 203 (1942).
[23] Bolland, Sundralingam, Sutton and Tristram, *Trans. Inst. Rubber Ind.* **17**, 29 (1941).
[24] Twyman and Allsopp, "Absorption Spectrophotometry", p. 67.

THE ELASTICITY OF A NETWORK OF LONG-CHAIN MOLECULES. II*

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On the basis of the kinetic theory of elasticity, Wall[1] has developed a statistical method for treating the problem of the elasticity of a three-dimensional network of long-chain molecules, and has applied it to the derivation of the stress-strain relations for the simplest types of deformation of rubberlike materials, namely, elongation, unidirectional compression and shear. The significance of Wall's theoretical approach has been discussed in some detail in an earlier paper[2], in which reasons were given for preferring Wall's method to the earlier attempts to solve this problem.

In the present paper the method of Wall is extended to the most general type of homogeneous deformation of rubberlike materials, of which those already considered by Wall are special cases. An expression is derived for the work of deformation, or *strain-energy* in the general case, and from this certain relations between the principal stresses and strains are obtained.

DERIVATION OF STRAIN-ENERGY FUNCTION

In a homogeneous deformation, the state of strain at all points of the deformed body is the same. It is defined as a displacement such that the coördinates of a point after the deformation are expressible as linear functions of the coördinates of the point before displacement. By homogeneous strain a sphere is transformed into an ellipsoid—the *strain ellipsoid*—of which the three principal axes are derived from three mutually perpendicular diameters of the sphere. In general, the directions of the principal axes differ from those of the diameters of the sphere from which they were derived; in the special case where they are the same the strain is said to be pure. Any homogeneous strain may be resolved into a pure strain plus a rotation[3]. When a suitably placed cube is subjected to homogeneous strain, it becomes a rectangular block (Figure 1) having sides of length λ_1, λ_2, λ_3, equal to the semiaxes of the strain ellipsoid, where $\lambda_1 - 1$, $\lambda_2 - 1$ and $\lambda_3 - 1$ are the principal extensions. The forces f_1, f_2, f_3 are normal to the surfaces of the block.

In applying the molecular theory to the derivation of the strain-energy function, the following assumptions are made[1].

1. The N molecules of the network all have the same chain length.
2. The distribution of lengths, *i.e.* end-to-end distances, of the molecules in the undeformed state is that given by Kuhn's statistical formula.
3. On deformation, the components of length of the individual molecules are changed in the same ratio as the corresponding dimensions of the bulk rubber.
4. The deformation takes place without change of volume.

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By postulate (3), a molecule whose original components of length were x, y and z will have the length-components $\lambda_1 x$, $\lambda_2 y$ and $\lambda_3 z$, after a deformation corresponding to a pure strain. Hence, if the original distribution of lengths is that given by Kuhn's formula, *i.e.*:

$$p(x, y, z)\,\mathrm{d}x\cdot\mathrm{d}y\cdot\mathrm{d}z = \frac{\beta^3}{\pi^{3/2}}\mathrm{e}^{-\beta^2(x^2+y^2+z^2)}\,\mathrm{d}x\cdot\mathrm{d}y\cdot\mathrm{d}z \qquad (1)$$

the distribution corresponding to the strained state will be:

$$p'(x, y, z)\,\mathrm{d}x\cdot\mathrm{d}y\cdot\mathrm{d}z = \frac{\beta^3}{\pi^{3/2}}\mathrm{e}^{-\beta^2(x^2/\lambda_1^2+y^2/\lambda_2^2+z^2/\lambda_3^2)}\,\mathrm{d}x\cdot\mathrm{d}y\cdot\mathrm{d}z \qquad (2)$$

Since the distribution is unaffected by a rotation, Formula (2) represents equally well any homogeneous strain. If n_i is the number of molecules in the

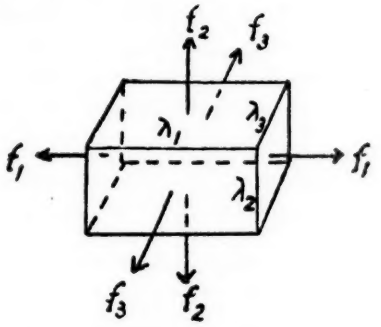

FIG. 1.—Homogeneous deformation of unit cube.

cell $\Delta x_i\cdot\Delta y_i\cdot\Delta z_i$ before deformation, and s_i the number in the same cell after deformation, the probability P of the distribution defined by (2) is related to the probability P_0 of the most probable state (1) by Wall's formula:

$$\ln(P/P_0) = \textstyle\sum_i s_i \ln(n_i/s_i) \qquad (3)$$

where

$$n_i = Np(x_i, y_i, z_i)\Delta x_i\Delta y_i\Delta z_i \quad \text{and} \quad s_i = Np'(x_i, y_i, z_i)\Delta x_i\Delta y_i\Delta z_i$$

Substitution of the appropriate values from (2) and (3) gives:

$$\ln(n_i/s_i) = -\beta^2[x^2(1 - 1/\lambda_1^2) + y^2(1 - 1/\lambda_2^2) + z^2(1 - 1/\lambda_3^2)]$$

and, therefore:

$$\ln(P/P_0) = -\beta^2[(1 - 1/\lambda_1^2)\Sigma s_i x_i^2 + (1 - 1/\lambda_3^2)\Sigma s_i y_i^2 + (1 - 1/\lambda_3^2)\Sigma s_i z_i^2) \qquad (4)$$

Now $\Sigma s_i x_i^2 = x^2$ where x^2 is the mean value of x^2 for the whole assembly of molecules. By integration it may be shown that, taking into account the relation (7) below, $x^2 = \lambda_1^2/2\beta^2$. Similarly $\overline{y^2} = \lambda_2^2/2\beta^2$ and $\overline{z^2} = \lambda_3^2/2\beta^2$. Hence, from (4):

$$\begin{aligned}\ln(P/P_0) &= -\tfrac{1}{2}N[(1 - 1/\lambda_1^2)\lambda_1^2 + (1 - 1/\lambda_2^2)\lambda_2^2 + (1 - 1/\lambda_3^2)\lambda_3^2)] \\ &= -\tfrac{1}{2}N(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3) \qquad (5)\end{aligned}$$

If W is the work of deformation per cc., *i.e.*, the strain-energy function, we may write $W = kT \ln (P/P_0)$, and, therefore:

$$W = \tfrac{1}{2}NkT(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3) \tag{6}$$

where N now represents the number of molecules per cc. This may be written in the alternative form:

$$W = \frac{\rho RT}{2M}(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3) \tag{6a}$$

where ρ is the density and M the molecular weight.

It will be seen that Equation (6) reduces to the special forms given by Wall for elongation and shear[4] on insertion of the appropriate values of λ_1, λ_2, and λ_3.

THE GENERAL STRESS–STRAIN RELATIONS

To obtain the stress-strain relations from Equation (6), it is necessary to consider a virtual displacement whereby the quantities λ_1, λ_2 and λ_3 are increased by $d\lambda_1$, $d\lambda_2$ and $d\lambda_3$. The corresponding increase in strain energy is then calculated from (6). But the work done in the displacement may also be stated in terms of the forces f_1, f_2 and f_3 (Figure 1), since the work done by the force f_i is $f_i d\lambda_i$. From the two expressions for the virtual work thus obtained the relation between the forces (or stresses) and the principal strains may be found.

The area of the face operated on by the force f_1 is $\lambda_2\lambda_3$, which is equal to $1/\lambda_1$, by the postulate of constancy of volume:

$$\lambda_1\lambda_2\lambda_3 = 1 \tag{7}$$

The stress S_1 on this face is, therefore, $\lambda_1 f_1$. Similarly, $S_2 = \lambda_2 f_2$ and $S_3 = \lambda_3 f_3$. Hence the work done by the forces in a small displacement is:

$$dW = \frac{S_1}{\lambda_1}d\lambda_1 + \frac{S_2}{\lambda_2}d\lambda_2 + \frac{S_3}{\lambda_3}d\lambda_3 \tag{8}$$

The relationship between the $d\lambda_i$ is obtained by differentiation of (7), *i.e.*:

$$\frac{d\lambda_3}{\lambda_3} = -\frac{d\lambda_1}{\lambda_1} - \frac{d\lambda_2}{\lambda_2}$$

which on substitution in (8) leads to the expression:

$$dW = (S_1 - S_3)\frac{d\lambda_1}{\lambda_1} + (S_2 - S_3)\frac{d\lambda_2}{\lambda_2} \tag{9}$$

in which λ_1 and λ_2 are independent variables which may have any values.

To obtain a second expression for dW, Equation (6) is written in the form:

$$W = \tfrac{1}{2}G(\lambda_1^2 + \lambda_2^2 + 1/\lambda_1^2\lambda_2^2 - 3)$$

where $G = NkT$. Whence, by differentiation:

$$dW = G(\lambda_1^2 - 1/\lambda_1^2\lambda_2^2)\frac{d\lambda_1}{\lambda_1} + G(\lambda_2^2 - 1/\lambda_1^2\lambda_2^2)\frac{d\lambda_2}{\lambda_2} \tag{10}$$

Combination of (9) and (10) leads to the stress-strain relations:

$$\begin{aligned} S_1 - S_3 &= G(\lambda_1^2 - \lambda_3^2) \\ S_2 - S_3 &= G(\lambda_2^2 - \lambda_3^2) \end{aligned} \tag{11}$$

GENERAL APPLICATION OF STRESS-STRAIN RELATIONS

The application of the formulas derived in the preceding paragraph to certain special problems will be considered in the next paragraph. In the present section some questions concrening the general applicability of Equations (11) will be discussed. Three cases need to be distinguished, and will be considered separately.

(*a*) *Given the Principal Strains, to find the Principal Stresses.*—Insertion of the given values of λ_i in Equations (11) leads to two simultaneous linear equations containing the three variables S_1, S_2 and S_3. It is, therefore, not possible to determine the stresses absolutely, but only the differences between any two. These are obtainable quite simply. This result means that if P_1, P_2 and P_3 are stresses satisfying Equations (11), then $S_1 = P_1 + p$, $S_2 = P_2 + p$, $S_3 = P_3 + p$ will also be a solution, that is to say, the strain is not affected by the superposition of a hydrostatic pressure. This is a direct consequence of postulate (4).

(*b*) *Given the Principal Stresses, to find the Principal Strains.*—This problem is rather more difficult than the preceding one. By insertion of the given values of S_i and writing $(S_1 - S_3)/G = a$, $(S_2 - S_3)/G = b$, Equations (11) become:

$$\lambda_1^2 - \lambda_3^2 = a, \quad \lambda_2^2 - \lambda_3^2 = b$$

Eliminating λ_1 and making use of the relation (7) gives:

$$\lambda_3^6 + (a + b)\lambda_3^4 + ab\lambda_3^2 - 1 = 0 \tag{12}$$

a cubic equation in λ_3^2 which may be solved by the usual methods.

(*c*) *Given the Applied Forces, to find the Principal Strains.*—In practice it is usually not the stresses but the forces which are given. Since $S_i = \lambda_i f_i$ the stresses can only be found when the strains are already known. Equations (11) must, therefore, be written in terms of the forces in the directions of the principal stresses, *i.e.*:

$$\begin{aligned} \lambda_1 f_1 - \lambda_3 f_3 &= G(\lambda_1^2 - \lambda_3^2) \\ \lambda_2 f_2 - \lambda_3 f_3 &= G(\lambda_2^2 - \lambda_3^2) \end{aligned} \tag{11a}$$

There is no general solution to these equations in simple analytical terms, but a solution to a particular problem may be obtained by graphical or approximate methods. In certain cases (as illustrated in the next paragraph) the equations reduce to a form in which a simple solution may be obtained algebraically.

APPLICATIONS OF EQUATIONS TO PARTICULAR PROBLEMS

The following examples are included to show how the general Equation (6) and the derived Equations (11) and (11*a*) may be applied to a number of problems of practical interest involving the elastic deformation of rubber.

(*a*) *Elongation or Unidirectional Compression.*—For an elongation (or compression) of the simplest type, we have $\lambda_1 = \alpha$, $\lambda_2 = \lambda_3 = \alpha^{-\frac{1}{2}}$, and $f_2 = f_3 = 0$. Therefore, from the first of Equations (11*a*):

$$f_1 = G(\alpha - 1/\alpha^2) \tag{13}$$

is the required relation between the applied force and the elongation ratio α. This expression was derived originally by Wall[1], by direct application of the statistical method.

(*b*) *Two-dimensional Extension.*—For an equal extension in two dimensions (as in an inflated balloon), the state of strain is the same as in the unidirectional compression. The system of forces differs from that in (*a*) by the addition of a negative hydrostatic stress system. The stress normal to the extended sheet (S_1) is zero, hence, from (11) the stress in the sheet is:

$$S_2 = S_3 = G(1/\alpha - \alpha^2)$$

where α is the ratio of the final to the original thickness. It is convenient to consider the force across a section of the sheet 1 cm. in length (analogous to surface tension). If this is denoted by t, then:

$$t = S_2\alpha = G(1 - \alpha^3) \qquad (14)$$

This shows that for moderately large extensions (*e.g.*, $\alpha < 1/3$) the tension in the sheet is independent of the extension.

(*c*) *Shear.*—Consider a sheet of rubber stretched in the direction OX by forces f_1, and let forces f_2 be applied in the direction OY of such magnitude that the dimension of the sheet in this direction remains unchanged (Figure 2).

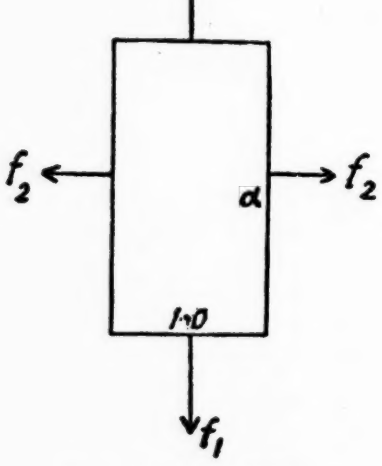

FIG. 2.—Rubber sheet in shear.

In this case, if we put $\lambda_1 = \alpha$, we have $\lambda_2 = 1$ and $\lambda_3 = 1/\alpha$, so that the state of strain is a shear. It is required to find the relation between the two principal stresses in the sheet and α, and also the relation between shear stress and shear strain.

Since the stress normal to the sheet is zero, $S_3 = 0$, and hence, from Equations (11):

$$\begin{matrix} S_1 = G(\alpha^2 - 1/\alpha^2) \\ S_2 = G(1 - 1/\alpha^2) \end{matrix} \quad \text{and} \quad \begin{matrix} f_1 = G(\alpha - 1/\alpha^3) \\ f_2 = G(1 - 1/\alpha^2) \end{matrix} \qquad (15)$$

It will be observed that the ratio of f_1 to f_2 is not constant, and that f_2 tends towards a constant value for large values of α. For small strains, *i.e.*, $\alpha \sim 1$, $df_1/d\alpha = 4G$, while $df_2/d\alpha = 2G$, and, therefore, $f_1 = 2f_2$. For a simple elongation, the initial value of $df_1/d\alpha$ is $3G$. Hence, comparing the tension in a simple elongation with the tension in the direction of α in what may be called a "shear elongation", it is seen that for small deformations the latter is greater than the former in the ratio 4/3, while for large deformations the two become equal.

To obtain the relation between shear stress and shear strain, use is made of the strain-energy function (6). This gives:

$$W = \tfrac{1}{2}G(\alpha^2 + 1/\alpha - 2) = \tfrac{1}{2}G\sigma^2 \tag{16}$$

where $\sigma(= \alpha - 1/\alpha)$ is the amount of the shear. As pointed out by Wall[1], this is equivalent to a linear relation between shear stress F_σ and shear strain of the form $F_\sigma = G\sigma$.

(*d*) *Elongation Plus Shear in Plane at Right Angles to Elongation.*—A problem of particular interest concerns the energy required to shear a body in the plane (y, z) after it has been given an initial elongation (or compression) in the direction OX. For the initial elongation, the strained dimensions of the unit cube are given by $\lambda_1 = \alpha$, $\lambda_2 = \lambda_3 = \alpha^{-\frac{1}{2}}$. With the superposition of a shear, these become $\lambda_1 = \alpha$, $\lambda_2 = \alpha^{-\frac{1}{2}}\beta$, $\lambda_3 = \alpha^{-\frac{1}{2}}/\beta$, the amount of the shear being $\sigma = \beta - 1/\beta$. From (7) the total work is:

$$W = \tfrac{1}{2}G(\alpha^2 + \beta^2/\alpha + 1/\alpha\beta^2 - 3)$$

The work due to the original elongation is:

$$W_\alpha = \tfrac{1}{2}G(\alpha^2 + 2/\alpha - 3)$$

The difference is the work due to the shear, *i.e.*:

$$W_\sigma = \tfrac{1}{2}G(\beta^2 - 2 + 1/\beta^2)/\alpha = \tfrac{1}{2}G\sigma^2/\alpha \tag{17}$$

This gives the interesting result that Hooke's Law is obeyed in shear in any plane at right angles to a simple elongation (or compression) but with an effective modulus of rigidity inversely proportional to the original elongation.

COMPARISON WITH MOONEY'S THEORY

The equations derived from the molecular theory, in particular Equation (6), resemble very closely the formulas derived by Mooney[5]. Mooney's argument is of a very general mathematical character, and takes no account of physical structure. His basic assumptions are: (1) that the material is isotropic, and after an elongation (or compression) it remains isotropic in a plane at right angles to the elongation; (2) that the traction, *i.e.*, shear stress, in simple shear in any isotropic plane is proportional to the shear (Hooke's Law); and (3) that there is no volume change on deformation. Mooney's expression for the strain energy is:

$$W = \frac{G}{4}\sum_{i=1}^{3}(\lambda_i - 1/\lambda_i)^2 + \frac{H}{4}\sum_{i=1}^{3}(\lambda_i^2 - 1/\lambda_i^2) \tag{18}$$

Equation (6), derived from the molecular theory, is a special case of (18), and is obtained therefrom by writing $G = H = NkT$. Again, the result represented by Equation (17) is a special case of Mooney's second assumption.

But whereas Mooney's theory leaves two constants, G and H, to be determined by the specific properties of the material, the molecular theory involves only one independent constant characteristic of the material for the description of the general elastic behavior of a rubber.

LIMITATION OF THEORY

It must be emphasized that the molecular network theory is limited in its practical application to rubber by the inadequacy of certain of its fundamental assumptions. The most serious discrepancy is likely to arise in connection with the assumption of Kuhn's distribution formula (1), which applies only as long as no important fraction of the molecules have lengths approaching the length of the fully extended chain. This will mean that the formula (6) will cease to be applicable when any one of the λ_i is large, *e.g.*, greater than about 5 in the case of a normal vulcanized natural rubber. To obtain the stress-strain relations for larger deformations, it would be necessary to make use of a more accurate expression than (1) for the distribution of molecular lengths. A beginning has been made by the derivation of a distribution function for paraffin molecules which is reasonably accurate over the whole range of molecular lengths[6].

SUMMARY

Wall's treatment of the elasticity of a molecular network is extended to cover the general homogeneous type of deformation of rubber. An equation is derived for the work of deformation in terms of the three principal strains, from which certain general stress-strain relations are deduced. These relations involve only one physical constant of the material. The use of the formulas is illustrated by their application to a number of simple cases. It is shown that the effective rigidity in respect of a shear in a plane at right angles to a previous elongation is inversely proportional to the elongation.

ACKNOWLEDGMENT

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REFERENCES

[1] Wall, *J. Chem. Physics* **10**, 485 (1942).
[2] Treloar, *Trans. Faraday Soc.* **39**, 36 (1943).
[3] For a fuller discussion of types of strain, reference should be made to textbooks on elasticity, *e.g.*, Love, "Mathematical Theory of Elasticity", Cambridge University Press, Chapter I.
[4] Treloar, *Trans. Faraday Soc.* **39**, 36 (1943); Equations (10) and (19).
[5] Mooney, *J. Applied Physics* **11**, 582 (1940).
[6] Treloar, work to be published in *Proc. Phys. Soc.*

SULFUR LINKAGE IN VULCANIZED RUBBERS *

I. REACTION OF METHYL IODIDE WITH SULFUR COMPOUNDS

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For many years the rubber chemist, in trying to explain the chemical nature of the vulcanization of rubber, was limited by two accepted theories: (1) Sulfur adds at the double bonds of the hydrocarbon, and (2) one atom of sulfur combines for each double bond saturated in the reaction. Therefore it was concluded that only one type of sulfur linkage would occur in vulcanizates. However, it was impossible on this basis to propose a hypothesis to account for all the facts. The few bits of direct evidence available have semed to support the theory of "one sulfur for each double bond saturated".

Since it is difficult to make any direct attack on this problem and since the art of vulcanization has far surpassed the science, it was not until 1938 that grave doubt was thrown on the generality of the "one sulfur atom per double bond saturated" theorem. The work of Brown and Hauser[1] indicated that there were wide variations in the number of sulfur atoms combined for each double bond saturated, depending on the type of acceleration used. Four years later Thornhill and Smith[2] pointed out that, in compounds containing reinforcing channel blacks, no loss of unsaturation could be detected on combination of sulfur during vulcanization. Thus the relation between sulfur combination and changes in unsaturation is at present obscure.

In addition, it is no longer considered probable that sulfur combination takes place primarily at the double bond. Sulfur itself does not readily add to the olefin double bond. Farmer and Michael[3], using as a model the attack of oxygen at the α-methylene carbon atom, suggest that sulfur also first combines at the reactive α-carbon and that any saturation of the double bond may be due to secondary reaction or addition of hydrogen sulfide. At present, therefore, it is not known where the sulfur attacks the rubber chain or whether there is a direct correlation between the primary combination of sulfur and saturation of double bonds.

There is thus no reason to suppose that all the combined sulfur in the vulcanizate is chemically linked in the same manner. On the contrary, the presence of two or more different types of sulfur linkages in vulcanized rubber would explain some hitherto obscure points—for instance, the lack of relation of combined sulfur to physical properties when different stocks are considered. The entire situation is pointed up by the need for determining the best methods of utilizing synthetic rubber—in particular, GR-S, whose vulcanization behavior is apparently quite different from natural rubber, especially in pure-gum types of compound. If it can be shown that, chemically, vulcanization of GR-S proceeds along those lines which give best results with rubber but that

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the resulting vulcanizate is not satisfactory, it would seem clear that future improvement must come either from wholly new vulcanization methods or from improved polymers.

The present investigation was started in an effort to get direct evidence as to the type of sulfur linkage in vulcanizates. It was felt that the type of sulfur bond was closely related to the desirable physical properties of high tensile strength and good aging.

The work of Geiger, Harris, Mizell, and coworkers[4] on wool has definitely established the disulfide cross-link as an important factor in the development of the elasticity and strength of this protein. They detail an instructive comparison of wool with rubber. Some of the reactions described in this article were also used by them in their study of the disulfide link.

The most promising line of investigation for a study of vulcanization appeared to be the action of alkyl halides on the sulfur atom in various linkages. It was first necessary to establish the background by a study of an alkyl halide; methyl iodide was chosen for its activity on simple sulfur compounds.

REACTION OF METHYL IODIDE

Methyl iodide was chosen as the reagent to investigate the sulfur linkage in vulcanizates, since its reactions with the sulfur atom differ in rate with the type of bond and the residues attached to it. The literature on sulfonium compounds and the theory of their reactions have been admirably summarized by Connor[5] and Levine[6].

The types of sulfur linkages which could be expected when sulfur reacts with a hydrocarbon such as rubber are listed below. The residues attached to the sulfur are designated R. These residues may be either aliphatic or alicyclic, or the sulfur may form part of a heterocyclic ring as in tetrahydrothiophene. For simplicity it is assumed that the influence of the type of hydrocarbon residue on the sulfur atom is fully determined by that part of the residue within four carbon atoms of the sulfur atom:

1. Mercaptans, R—SH. R may be alkyl, allyl, or vinyl.
2. Sulfides, R—S—R. R may be alkyl, allyl, vinyl, or heterocyclic in a saturated ring.
3. Polysulfides, R—Sx—R where x = 2, 3, etc., may be cyclic-saturated, linear-saturated, linear-unsaturated.
4. Heterocyclic unsaturated rings such as thiophene or acetylene sulfide.

There has never been any experimental proof of Erdmann's thioözonides or cyclic polysulfides (case 3 above, $x = 3$)[7]. The sulfur atom in a sulfonium compound is considered to have four bonds: two covalent, one coördinate-covalent, and one electrovalent. Several workers, however, have suggested sulfur compounds showing sulfur with three or even four covalent bonds on carbon[8]. While sulfur with two covalent bonds and one coördinate-covalent bond with carbon is known[9], these compounds are very unstable. Sulfur with two covalent and two coördinate-covalent bonds with carbon has not been shown to exist. Any of the sulfur linkages listed above except the mercaptan type could exist either intra- or intermolecularly with reference to the rubber hydrocarbon chain.

The reactions of methyl iodide with various members of these four classes were studied in an effort to work out a quantitative analytical scheme. Its

reaction with a mercaptan might be expected to proceed as follows; this reaction is well known in 95% ethanol in presence of sodium hydroxide:

$$C_3H_7SH + 2CH_3I \rightarrow HI + C_3H_7(CH_3)_2SI \quad (1)$$

Meyer and Hohenemser[10] have claimed that the mercaptan group is not attacked by methyl iodide at room temperatures in the dark. On attempting to confirm this, a noticeable evolution of hydrogen iodide occurred when *n*-propyl mercaptan reacted with an excess of methyl iodide under nitrogen in the dark. When the excess reagent and unreacted material were evaporated off, a solid residue was left, probably the dimethyl *n*-propyl sulfonium iodide. The reaction is about 11% complete after 68 hours, judged from the weight of the residue. The materials used were carefully purified as described later in the experimental section. If an equal volume of ethanol is added to the methyl iodide, the reaction speed is doubled (Figure 1). In addition to this

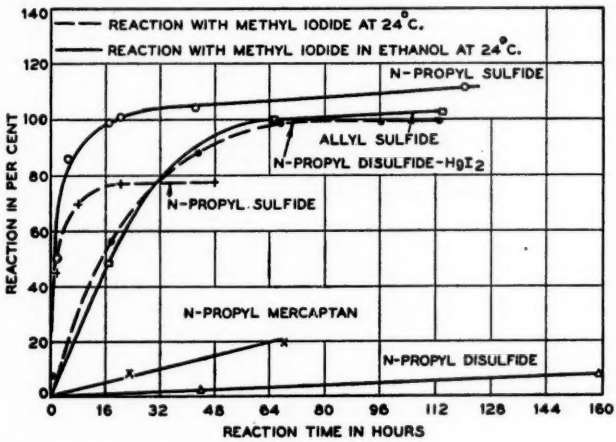


FIG. 1.—Percentage reaction *vs.* time for reaction of methyl iodide and various sulfur compounds.

reaction, there will be a further very fast reaction if any free iodine is produced; this might occur if a mixture of a disulfide and a mercaptan were reacted with methyl iodide. This oxidation of the mercaptan would occur:

$$2C_3H_7SH + I_2 \rightarrow (C_3H_7)_2S_2 + 2HI \text{ (very fast)} \quad (2)$$

$$(C_3H_7)_2S_2 + 4CH_3I \rightarrow 2(C_3H_7)(CH_3)_2SI + I_2 \text{ (slow)} \quad (3)$$

Summing up:

$$2C_3H_7SH + 4CH_3I \rightarrow 2(C_3H_7)(CH_3)_2SI + 2HI \quad (4)$$

Equation 4 would occur only after a fairly long time, since 3 is slow. Reaction 3 is discussed below. In any case, the presence of mercaptan would be indicated by production of hydrogen iodide. Actually no hydrogen iodide was ever detected in the methyl iodide reaction with vulcanizates. There is, however, the possibility that at elevated temperatures any hydrogen iodide produced would give hydrogen sulfide as follows[11]:

$$RSH + HI \rightarrow RI + H_2S \quad (5)$$

Actually, small amounts of hydrogen sulfide are produced when methyl iodide reacts with certain vulcanizates.

FORMATION OF SULFONIUM SALTS

The addition of methyl iodide to organic sulfides with the formation of sulfonium salts has been known for eighty years and studied at frequent intervals during that time without exhausting the subject. The reaction proceeds thus:

$$C_3H_7S—C_3H_7 + CH_3I \rightarrow (C_3H_7)_2CH_3SI \quad (6)$$

No data on the rate of reaction at room temperature could be found except the statement by Brown and Hauser[12] that the reaction with *n*-butyl sulfide was quantitative in 48 hours when the sulfide had been diffused into a crude rubber sample. This claim has been confirmed and will be described later. When, however, the simple system *n*-propyl sulfide-methyl iodide was investigated, it was found that 78–80% was the maximum yield obtainable (Figure 1). This yield was calculated on the basis of Equation 6. The product was increasingly yellow with increase in reaction time. The melting point was identical with that of the methyl di-*n*-propyl sulfonium iodide isolated from the same reaction in ethanol. No explanation is offered for the difference in yield here and in ethanol solution.

The use of methanol or ethanol as solvent is reported to give the best yields of sulfonium salts[13]. When the reaction was carried out with *n*-propyl sulfide in equal volumes of methyl iodide and ethanol, the yield was quantitative in about 17 hours. The time *vs.* yield data at room temperature are shown in Figure 1. On long standing in air over 17 hours, decomposition occurs and the product is colored a red-brown from free iodine with a corresponding increase in yield over 100%. This decomposition could be stopped completely if the reaction was carried out in the absence of oxygen. The sulfonium salt indicated in Equation 6 was isolated, purified, and analyzed following the procedures of Bost and Everett[13]. The analysis (Table I) showed it to be methyl di-*n*-propyl sulfonium iodide. The melting point or, more appropriately, decomposition point varied with pressure as shown in Table I.

TABLE I

PROPERTIES OF SULFONIUM COMPOUNDS

Compound	Iodine, (percentage) Found	Iodine, (percentage) Calcd.	Weight taken, (Gram)	Milliequivalent $AgNO_3$ Used	Milliequivalent $AgNO_3$ Calcd.	Melting point (° C)
$(CH_3)_3SI$	59.8	62.2	0.1123	0.559	0.551	206 (decompd.)
$(C_3H_7)_2CH_3SI$	...	...	0.2341	0.899	0.899	115.7[a]

[a] Melting point varies with pressure: in vacuo 122.5, in air 115.7, in sealed tube 111.6.

Bost and Conn[14] report the formation of the analogous sulfonium salt from the cyclic compound, tetramethylene sulfide, and methyl iodide in heptane within 24 hours. Thus the cyclic or linear character of the saturated hydrocarbon residues on the sulfur atom does not seem to affect the reaction rate to any large extent.

Heavy metals salts, such as those of mercury, iron, zinc, and cadmium[15], increase the reaction rate, producing complexes of one or two molecules of the metallic salt with one molecule of the sulfonium compound. For example, the reaction of methyl iodide with dimethyl sulfide in the presence of mercuric iodide at room temperature is complete in one hour[16].

The same experiments were carried out with allyl sulfide. This would be expected to give methyldiallylsulfonium iodide according to the reaction of Equation 6. The per cent yield *vs.* reaction-time data are plotted in Figure 1. The reaction is slower than with *n*-propyl sulfide. There is, however, a great difference in the allyl and *n*-propyl sulfide reactions with methyl iodide. The product isolated is not methyldiallylsulfonium iodide but trimethyl sulfonium iodide. The reaction curve in Figure 1 is calculated on this basis, since the analysis of the product isolated corresponds to that of trimethylsulfonium iodide as shown in Table I. Parr bomb analysis for iodine confirmed the Volhard titration data. The reaction mixture was colored red-brown from the free iodine liberated in the reaction. These results can be explained on the basis of the molecular decomposition mechanism proposed by Ray and Levine[17].

$$(C_3H_5)_2S + CH_3I \rightleftarrows (C_3H_5)_2CH_3SI \text{ (unstable)} \quad (7)$$

$$(C_3H_5)_2CH_3SI \rightleftarrows C_3H_5SCH_3 + C_3H_5I \quad (8)$$

$$C_3H_5SCH_3 + CH_3I \rightleftarrows (C_3H_5)(CH_3)_2SI \text{ (unstable)} \quad (9)$$

$$C_3H_5(CH_3)_2SI \rightleftarrows CH_3SCH_3 + C_3H_5I \quad (10)$$

$$CH_3SCH_3 + CH_3I \rightarrow (CH_3)_3SI \quad (11)$$

Summing up:

$$(C_3H_5)_2S + 3CH_3I \rightarrow 2C_3H_5I + (CH_3)_3SI \quad (12)$$

In some cases the iodide formed is unstable, and the two hydrocarbon residues unite:

$$2C_3H_5I \rightarrow I_2 + (C_3H_5)_2 \quad (13)$$

or rewriting Equation 12:

$$(C_3H_5)_2S + 3CH_3I \rightarrow I_2 + (C_3H_5)_2 + (CH_3)_3SI \quad (14)$$

With allyl sulfide, step 13 must take place, since free iodine is observed. The conclusion can be made then, that in ethanol solution, sulfonium compounds containing allyl residues are not stable toward methyl iodide. The mercuric iodide-catalyzed reaction yields trimethylsulfonium iodide-mercuric iodide complex in the same way. This successive splitting off of hydrocarbon residues until only the simplest, *i.e.*, methyl, is left is also shown by aromatic sulfides. Backer and Stedehouder[18] found that at room temperatures both benzyl sulfide and disulfide gave trimethylsulfonium iodide after a few days of reaction with methyl iodide.

MERCURIC IODIDE AS CATALYST

In 1904 Hilditch and Smiles[19] found that the reaction of methyl iodide with alkyl disulfide was very slow at room temperature but that, on addition of mercuric iodide, the reaction was rapid, giving mercuric iodide complexes. The mechanism of these reactions was further investigated by Steinkopf and Müller[20] in 1923.

In 1940 Haas and Dougherty[21] proposed the most satisfactory mechanism to date to explain the products obtained. A short study of the uncatalyzed reaction, using *n*-propyl disulfide, carried out in the present research, confirmed the previous workers' comments on the sluggishness of the uncatalyzed reaction:

$$C_3H_7—S—S—C_3H_7 + 4CH_3I \rightarrow 2(CH_3)_2C_3H_7SI + I_2 \quad (15)$$

The reaction was followed by titrating the iodine liberated. Mercuric iodide is a better catalyst than mercuric chloride. The slow reaction is shown by the curve in Figure 1.

One experiment was performed to determine whether the reaction of methyl iodide with the sulfide linkage was impeded by the presence of disulfide. Equal amounts of *n*-propyl sulfide and disulfide were placed in methyl iodide-ethanol mixture in nitrogen for 23 hours. After evaporation of disulfide, methyl iodide, and ethanol the residue was 98% of the theoretical, calculated from Equation 6. This would indicate that the sulfide linkage may be successfully determined in the presence of the disulfide by methyl iodide.

The mercuric iodide catalyzed reaction was then carried out with the same disulfide. Haas and Dougherty[21] studied this reaction in detail:

$$C_3H_7S{-}SC_3H_7 + CH_3I + HgI_2 \rightarrow C_3H_7{-}\underset{\displaystyle I}{\underset{|}{S}}{-}\underset{\displaystyle CH_3}{\underset{|}{S}}{-}C_3H_7.HgI_2 \text{ (unstable)} \quad (16)$$

$$C_3H_7{-}\underset{\displaystyle I}{\underset{|}{S}}{-}\underset{\displaystyle CH_3}{\underset{|}{S}}{-}C_3H_7.HgI_2 \rightarrow C_3H_7SI + CH_3{-}S{-}C_3H_7.HgI_2 \quad (17)$$

$$CH_3{-}S{-}C_3H_7.HgI_2 + CH_3I \rightarrow (CH_3)_2C_3H_7SI.HgI_2 \quad (18)$$

$$C_3H_7SI + CH_3I \rightarrow C_3H_7CH_3SI_2 \quad (19)$$

$$C_3H_7CH_3SI_2 + HgI_2 \rightarrow C_3H_7{-}S{-}CH_3.HgI_2 + I_2 \quad (20)$$

$$C_3H_7S{-}CH_3.HgI_2 + CH_3I \rightarrow C_3H_7(CH_3)_2SI.HgI_2 \quad (21)$$

Summing up:

$$C_3H_7{-}S{-}S{-}C_3H_7 + 4CH_3I + 2HgI_2 \rightarrow 2(C_3H_7)(CH_3)_2SI.HgI_2 + I_2 \quad (22)$$

Under the experimental conditions described below, the reaction was followed by titration of the iodine liberated. Since the addition of ethanol retarded the reaction, no solvent was used in these experiments. The reaction rate curve is shown in Figure 1. The same results are obtainable either in air or nitrogen. The mercuric iodide-catalyzed reaction of methyl iodide with *n*-propyl disulfide is substantially complete in 68 hours, while in the same time the uncatalyzed reaction gives only 3.5% reaction. Rây and Adhikari[16] claim that, in the analogous reaction with a polysulfide such as di-*n*-propyl trisulfide, the sulfur bonds are broken and the same sulfonium-mercuric iodide complexes result as with disulfides.

Bost and Conn[14] reported that thiophene does not give an addition product with methyl iodide or with mercuric iodide. Under the conditions used in the above experiments this has been confirmed.

REACTIONS OF RUBBERS WITH METHYL IODIDE

Meyer and Hohenemser[10] stated that treatment of rubber with methyl iodide at room temperature did not produce any chemical change in the rubber. Both acetone-extracted pale crepe and a GR-S of low gel content were placed in methyl iodide for 72 hours. Both rubbers swelled considerably, the GR-S losing all shape. On evacuation of the reagent at room temperature the rubbers showed a weight gain of 0.8 to 1%. This gain could be eliminated by heating the rubber 2 hours at 60° C in a vacuum. It is evident, then, that very little, if any, reaction takes place between crude rubbers and methyl iodide. Work on the reaction of the sulfur originally present in the GR-S itself is in progress.

The reaction of methyl iodide with *n*-propyl sulfide was carried out after the sulfide had diffused into acetone-extracted pale crepe. After 17 hours a yield of 99.2% as measured by the weight gain of the rubber, was obtained. This confirms the work of Meyer and Hohenemser[10] and Brown and Hauser[12]. The rubber does not inhibit the sulfide-methyl iodide reaction.

The analogous experiment with the methyl iodide-disulfide reaction in the presence of mercuric iodide was carried out with the *n*-propyl disulfide diffused into the rubber. Methyl iodide and mercuric iodide were then added and the liberated iodine was titrated. After 144 hours, only 75% of the theoretical yield of iodine could be titrated. This was thought to be due to physical retention of the iodine by the rubber since, even after titration, the rubber gave up more free iodine when soaked in carbon disulfide.

CONCLUSIONS

1. Mercaptans react slowly with methyl iodide to give the characteristic product, hydrogen iodide.
2. Sulfides react quantitatively at room temperature in 1–3 days, but the product depends on the type of hydrocarbon residues.
3. Splitting of the sulfur-carbon bond of a sulfide on reaction with methyl iodide takes place when the hydrocarbon residues on the sulfur are electronegative in nature, *i.e.*, contain double bonds, phenyl groups, etc.
4. Disulfides react very slowly with methyl iodide and, in so doing, break the disulfide linkage, with liberation of free iodine.
5. Sulfide can be determined in the presence of disulfide in 24 hours by the weight gain of the reaction vessel after the excess of methyl iodide has been evaporated.
6. Mercuric iodide catalyzes the sulfide and disulfide reactions; the former is quantitative in 1 hour, and the latter in 3 days at room temperature.
7. Methyl iodide does not react with thiophene, probably because of the pronounced electronegative character of the two double bonds in the aromatic type of ring.
8. Rubber does not interfere in the reactions of methyl iodide with sulfur compounds in the chemical sense. However, difficulties may be encountered, such as slowing up of reactions due to dependence on diffusion rate, available surface, and other physical factors.

EXPERIMENTAL DETAILS

Purity of reagents.—The sulfur compounds were Eastman organic chemicals. The methyl iodide and mercuric iodide were Mallinckrodt's analytical reagents. Except where indicated, the compounds were purified by fractionation in the 0.5-inch-diameter, helix-packed column A, with 24 inches of packed length and with silvered vacuum and heated air jackets. The helices were single turn, 1 mm. inside diameter and 2 mm. outside diameter. The column tested twenty-six plates at a reflux rate of 200 cc. per hour. The fractionations were carried out at a reflux ratio of 20 : 1. Only the middle third of the distillate was used and that only if the boiling point was constant within 0.1° C. *n*-Propyl disulfide was distilled at 54.7 ± 0.1 mm. in column A. The physical properties of the purified compounds are given in Table II.

The methyl iodide was first shaken with mercury to remove free iodine if present, dried over Drierite for 2 days, and distilled in the 1-inch helix-packed column B, with 25 inches of packed length and a silvered vacuum jacket. Column B tested twenty plates. The methyl iodide was stored in a brown glass-stoppered bottle in the dark. For those experiments in which mercuric iodide was used, the distillation was omitted; the free iodine was simply removed with mercury and filtered. No decomposition was noticed in any fractionated methyl iodide.

TABLE II

PHYSICAL PROPERTIES OF PURIFIED COMPOUNDS

Compound	Boiling point (° C)	Pressure (Mm. Hg)	n_D^{25}	d_4^{25}
n-Propyl mercaptan				
Present work	.....	...	1.4353	0.8358
Literature[22]	67.4–.5	760	1.4351	0.8357
n-Propyl sulfide				
Present work	142.4–.5	760	1.4462	0.8332
Literature[23]	141.6–142.1	749	1.4456	0.8319
Allyl sulfide				
Present work	138.6	751.2	1.4870	....
Literature[24]	138.6	758.3	1.4877[a]	....
n-Propyl disulfide				
Present work	110.6	54.7	1.4980[b]	0.9598[b]
Literature[25]	191.2	760	1.4981[b]	0.9525[b]
Methyl iodide				
Present work	42.52	760	1.5306[b]	2.2813[b]
Literature[26]	42.6	760	1.5307[b]	....

[a] At 26.8° C [b] At 20° C

Procedure and apparatus.—0.2 gram of the sulfur compound was weighed into 125-cc. ground joint flask *A* (Figure 2). The required volume of methyl iodide and ethanol, usually 10 cc. of each, was added, and the flask attached to the stopcock-ground joint assembly *C* if the run was to be made under nitrogen. If not, the flask was simply closed with a ground joint stopper and placed in the dark at 24° C. The assembly used in the nitrogen runs had been previously attached to the manifold by another ground joint as shown. The upper quarter inch of the flask joint was greased so that a vacuum seal could be obtained without contamination of the contents of the flask. The manifold had five male joints and the appropriate connections so that an entire series of experiments could be prepared at one time. After the flask was attached by steel springs to the assembly on the manifold, a Dewar flask containing liquid nitrogen was slipped around it and the contents frozen. Evacuation was then begun by a Hyvac pump, using a liquid nitrogen trap. After the pressure had reached 10^{-3} mm. of mercury, as shown by the absence of a discharge across the neon sign electrodes in the system, the flask was rinsed twice with prepurified nitrogen with successive evacuations. The Dewar flask was then removed, the contents allowed to warm to room temperature, prepurified nitrogen added to atmospheric pressure, the assembly stopcock closed, and the flask with assembly removed from the manifold and stored in the dark in a constant-temperature room at 24° C.

The water-pumped prepurified nitrogen obtained from the Air Reduction Sales Company was guaranteed to have an oxygen and water content of no more than 0.001% each. Those experiments which called simply for titration of the iodine liberated were merely opened at the end of the set reaction time and titrated. In cases where the weight of the solid product was wanted, the flask was again frozen in liquid nitrogen and evacuated. On removal of the liquid nitrogen, flask A was connected through a large-bore stopcock to an evacuated trap, *B*, cooled with liquid nitrogen on the next position in the manifold (Figure 2). The excess reagent and solvent were thus distilled off under vacuum at room temperature, leaving the solid product in the original flask which was then weighed after careful cleaning of the exterior. Where the experiments were run in air and the weight gain was desired, the same

procedure for vacuum distillation of solvent, etc., was followed as given for the nitrogen runs. The distillate was always examined for iodine, hydrogen iodide, and hydrogen sulfide.

n-Propyl mercaptan.—An effort was made to purify Eastman *n*-propyl mercaptan in column A. The distillate, however, analyzed by the iodine method[27], was only 95% mercaptan. The mercaptan was then purified chem-

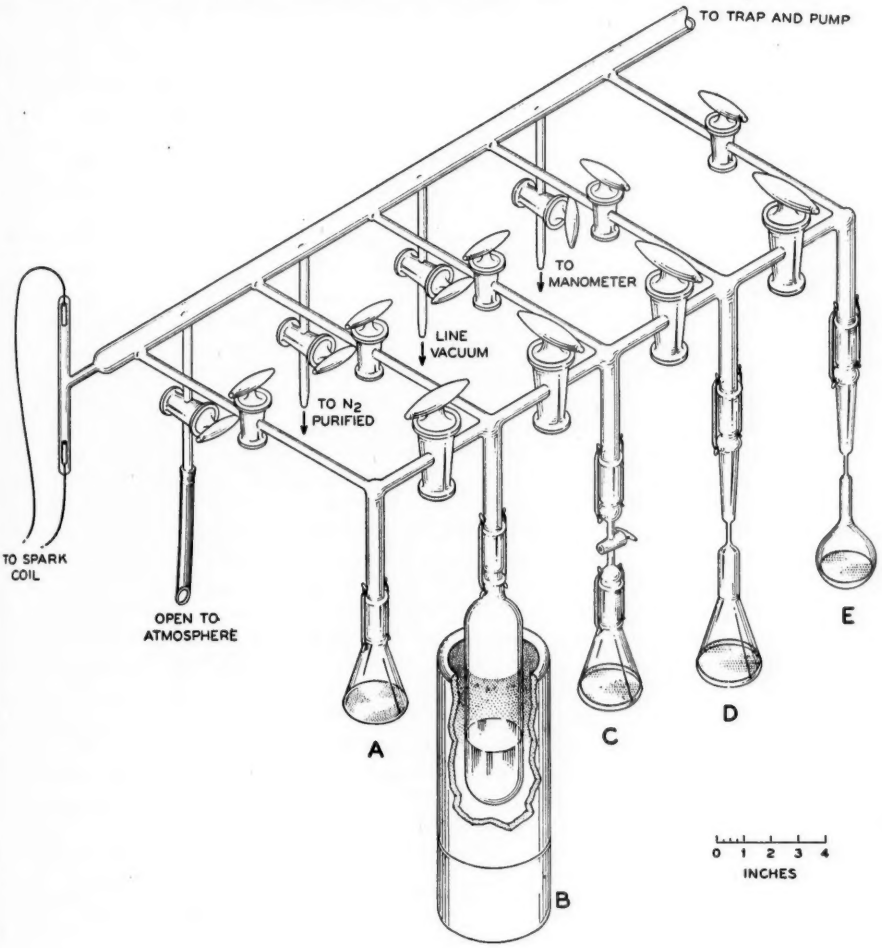


FIG. 2.—Manifold showing special flasks and assembly in use.

ically, as suggested by Ellis and Reid[22]. For reaction rate measurements, 0.2 gram of *n*-propyl mercaptan was dissolved in 10 cc. (22.8 grams) of methyl iodide, and in some experiments 10 cc. of ethanol was added. The runs were made under nitrogen. When methyl iodide alone was used, the solution turned yellow after 15 hours and a yellow oil separated. When ethanol was used, the solution remained colorless. On evaporation of excess reagents and solvents, a yellow oily material was left. In all cases hydrogen iodide was present after

some hours of reaction. When mercuric iodide was used and the reaction mixture diluted with ethanol, yellow crystals were obtained together with liberation of much hydrogen iodide.

n-Propyl sulfide.—Methyl iodide reacts very quickly with *n*-propyl sulfide. One hour after the addition of 0.2 gram to 10 cc. of methyl iodide to form a clear solution, a yellow oil starts to collect on the surface. This oil is methyl di-*n*-propyl sulfonium iodide. After evaporation of the solution, it is left as white-yellow crystals, whose melting behavior is shown in Table II. If the reaction mixture is allowed to stand in air for periods over 24 hours, it turns brown-red, due to free iodine. Ethanol gives better yields than neohexane. The solid reaction product was reprecipitated from ethanol with ether. The experiments described with *n*-propyl sulfide were all run in air.

Allyl sulfide.—Immediately after purification by fractionation in column A, the allyl sulfide was reacted with methyl iodide-ethanol mixture under nitrogen —0.2 gram in 10 cc. methyl iodide (22.8 grams) plus 10 cc. ethanol. The solution turned yellow-brown from free iodine in the first 20 hours. After 30 hours large platelike crystals of trimethylsulfonium iodide appeared. Analysis of the crystals is shown in Table I.

n-Propyl disulfide.—Purification was by vacuum fractionation. Several preliminary experiments were necessary to establish optimum conditions of reaction; 0.2 gram of disulfide with 10 cc. of methyl iodide and 10 cc. of ethanol were finally settled upon for direct comparison with the *n*-propyl sulfide reaction. The reaction was run under nitrogen without a heavy metal catalyst. It proceeded slowly. It was followed by titration of the free iodine present with 0.1 *N* aqueous thiosulfate. To maintain one phase, 50 cc. of ethanol was added before titration. Starch indicator could not be used in these solutions. Instead, the solution was titrated to a clear, light yellow end point, which was recognized without difficulty after a few preliminary trials. At the end point the solution turned from a brilliant yellow to a flat light yellow.

n-Propyl disulfide with mercuric iodide.—The optimum conditions involved the use of 0.2-gram portions of *n*-propyl disulfide with twice the theoretical weight of mercuric iodide (2.42 grams) in 10 cc. (22.8 grams) of methyl iodide under nitrogen. Mercuric iodide is soluble to the extent of 3.7 grams per 100 grams of methyl iodide at room temperature. The reaction mixture gradually turns red-brown. The reaction was followed by iodine titration, as described for the uncatalyzed reaction. Results were duplicable, whether the reaction was run under nitrogen or air. Several qualitative experiments were performed to determine whether any combination of the following compounds—methyl iodide, ethanol, *n*-propyl sulfide, mercuric iodide, and methyl di-*n*-propyl sulfonium iodide—would produce free iodine under the same conditions as the disulfide-mercuric iodide reaction did. No free iodine was produced with any combination.

Thiophene.—Eastman's organic chemical grade was used without purification. No solid was found on evaporation after standing with methyl iodide, with or without mercuric iodide, for 72 hours.

II. REACTION OF METHYL IODIDE WITH VULCANIZATES

In Part I the reactions of methyl iodide with simple sulfur compounds were studied with the intent of using the wide difference in reaction rates to investigate the sulfur linkages in vulcanized rubber. This article will detail the

application of the methyl iodide reaction to various natural and synthetic rubber stocks.

The complexity of the vulcanization process is shown by the number of theories in the recent literature[28]. It is proper to consider first some of the evidence commonly cited against the hypothesis that the intermolecular combination of sulfur with rubber is the prime cause of vulcanization. The work of Williams[29] has been mentioned many times in this connection. Williams reported peptization of a di-*o*-tolylguanidine-accelerated gum rubber stock in 5% piperidine-toluene solution at 97° C in 24 hours, in the absence of oxygen. If this claim can be confirmed, it is difficult to see how it can be explained by those who regard vulcanization as resulting from the cross-linking of linear polyisoprene chains with sulfur. For this reason a short investigation was undertaken to determine the solubility behavior of vulcanizates with regard to oxygen.

DEPENDENCE OF PEPTIZATION ON OXYGEN

The di-*o*-tolylguanidine gum stock of Williams consisted of 100 parts smoked sheet, 3 sulfur, 2 zinc oxide, and 1 di-*o*-tolylguanidine; it was cured 30 minutes at 141.6° C. This acetone-extracted stock was immersed in a steam bath with 5% piperidine-toluene solution in air (1 gram rubber to 20 cc. solution). In 48 hours a clear orange-red viscous dispersion was obtained. This experiment was repeated in the absence of oxygen. The glass tube containing the rubber and solution was cooled in dry ice during initial evacuation. The tube was warmed and boiled under the vacuum of a Hyvac pump to drive off dissolved gases. This was repeated three times. A dry ice condenser on the long neck of the tubes prevented loss of either component. The tubes were then sealed off. Despite the vacuum in the tubes, the temperature maintained in them during immersion in the steam bath was 100° C, since shortly after the start of the experiment the solvent ceased to boil because a large proportion of it was bound by the swollen rubber. Although the experiment was carried on for more than 250 hours and the rubber underwent disintegration of gross structure, no clear solution was formed. A slimy mass of rubber remained and, on cooling, the sides of the tube became thickly coated with rubber.

It was found that an antioxidant such as phenyl-α-naphthylamine would accelerate the peptization of rubber when heated in air. The same accelerating effect is obtained by omitting the acetone extraction. This is probably due to di-*o*-tolylguanidine, the accelerator[31]. If the same acetone-extracted stock is heated in air in pure toluene for 340 hours, a cloudy yellow-orange dispersion results. In accordance with Williams' reported inability to peptize a stock accelerated with tetramethylthiuram disulfide, it was found impossible to make a dispersion from a mercaptobenzothiazole-accelerated stock by heating in air. The conclusion can be drawn that the Williams type of peptization of vulcanized rubbers is due to oxygen breakdown of the rubber, catalyzed by either natural or added accelerators or antioxidants.

Another case of peptization of vulcanized rubber under much more severe conditions is that in *p*-dichlorobenzene, usually carried out before unsaturation determinations are made[32]. Tire tread stock SB6 (Table I) was extracted with acetone-chloroform; 50-mg. samples were heated with 25-gram portions of *p*-dichlorobenzene in 125-cc. Erlenmeyer flasks on a hot plate at 174° C. One flask was left open to the air, one was evacuated, and one was filled with purified nitrogen. The latter two were glass-sealed after precautions had been taken

to remove oxygen by sweeping with purified nitrogen and evacuating with a Hyvac pump through a liquid air trap on the manifold described in Part I. Finely divided rubber was prepared by first "crumbing" the vulcanizate on tight, cold, mill rolls followed by chopping in a modified Sunbeam meat chopper. Only those particles which passed a U. S. 40-mesh sieve were retained. The sample in air dissolved in 80 minutes; the sample in vacuo and nitrogen did not disperse even on heating 24 hours or more. The samples which had failed to dissolve at 174° C in the absence of oxygen were then placed, still sealed, in an oven at 220° C; after heating 8 hours more, a black dispersion was obtained. This accelerating effect of oxygen on the dissolution of vulcanizates in *p*-dichlorobenzene was mentioned by Brown and Hauser[12], who found that it took approximately three times as long to dissolve the vulcanizates when heated in a stream of nitrogen as in air. The high-temperature dispersion of vulcanizates at 220° C can be adequately explained by rupture of primary valence links in the swollen gel as set forth by Tobolsky[33].

Apparently, then, the peptization of a sulfur-vulcanized rubber at moderate temperatures in a solvent which does not attack sulfur linkages is dependent on oxygen degradation of the rubber rather than on the simple solution of molecules held together by secondary forces. The same explanation has been given for the transformation of gel rubber into sol rubber by traces of oxygen[34].

Thus, the theory that the intermolecular combination of sulfur with rubber is responsible for vulcanization is not negated by the observation that certain vulcanizates are dispersable in the solvents studied, in the presence of oxygen.

REACTION OF METHYL IODIDE WITH VULCANIZATES

Meyer and Hohenemser[10] in 1935 were the first to suggest the use of methyl iodide for studying the types of sulfur links present in rubber vulcanizates. Their procedure was to let the vulcanizate stand 2 or 3 days in air in the dark with an excess of methyl iodide, evaporate in vacuum, wash with petroleum ether, and determine the iodine content of the rubber. Each iodine atom was assumed to represent one thioether link (Equation 6 in Part I). From 80 to 90% of the combined sulfur seemed to be present as thioether links, judged from their results.

In 1938 Brown and Hauser[12] applied the methyl iodide reaction to a series of compounds. Their values of thioether sulfur account for 20 to 60% of the combined sulfur at any given time of cure. The thioether sulfur, determined by the Meyer and Hohenemser method, was found to have no correlation with the physical properties of the stocks. They concluded that methyl iodide may also react with other sulfur compounds, that side reactions are present in the reaction with vulcanizates, and that "it is extremely doubtful that the methyl iodide test is sufficiently reliable for the study of sulfur linkages produced in vulcanization". All the standard tests for different sulfur links, when applied to rubber dispersed in *p*-dichlorobenzene diluted with carbon tetrachloride, gave negative results.

In 1941 a patent was granted to Smallwood[35] for conversion products obtained by heating crude or vulcanized rubber at 70° to 170° C in the presence of aliphatic halides. It is claimed that vulcanized rubber is changed to either a balatalike material or to one which resembles shellac. Of special interest here is the claim that 80–90% of the sulfur originally combined with the rubber may be removed in the form of sulfonium compounds or thioethers by treatment with methyl iodide at elevated temperatures.

With the reactions of methyl iodide and simple sulfur compounds as a guide, it was hoped that the behavior of sulfur vulcanizates toward this reagent could be interpreted on a more rational basis than had been possible heretofore. The same technique of carrying out the reactions was used with the vulcanizates as described in the preceding paper for the sulfur compounds, with certain modifications described in the experimental section later. All reactions were run under purified nitrogen to eliminate decomposition of methyl iodide and any other complicating effects of oxygen. The runs made at 50° and 100° C required special flasks which could be glass-sealed (Figure 2 in Part I). After

TABLE I

STOCK RECIPES

Stock	Pale crepe	GR-S	Tube sulfur	Zinc oxide	Stearic acid	Diphenyl-guanidine	Tetra-methyl-thiuram disulfide	Mer-capto-benzo-thiazole	Channel black
SB1A	100	...	8.0	...	...	....	...	...	..
SB2	100	...	2.5	5	0.5	1	...	...	..
SB3	100	...	8.0	5	...	....	...	...	..
SB4	100	...	2.5	5	0.5	....	0.25	...	..
SB5	...	100	2.5	5	0.5	1	...	...	..
SB6	100	...	2.5	5	2.0	....	0.50	...	50
SB7	100	...	2.5	5	0.5	0.0625	...	...	..
SB8	100	...	3.0	5	4.0	....	...	1	45
SB9	100	...	3.0	5	4.0	....	...	1	→
SB10	...	100	3.0	5	...	....	...	1	..
SB11	...	100	3.0	5	...	....	...	1	45
SB12	100	...	...	5	0.5	....	2.0	...	..

TABLE II

PHYSICAL AND CHEMICAL CHARACTERISTICS OF RUBBERS AND STOCKS

	Optimum cure (min.)	Combined S (G. per 100 g. rubber)	Combined S (Per cent)	Tensile strength (lb./sq. in.)	Elongation at break (%)	Acetone-chloroform extracted stocks: Loss (%)	Combined S (%)	Unsaturation[a] (%)	Percentage of original combined S remaining[b]
Optimum cure at 141.6° C									
Pale crepe	..	0	..	..	..	3.0[c]	0	96.8	..
GR-S	..	0.19	..	..	..	10.1[c]	0.19	99.2	68.4
SB1A	240	4.06	3.76	3190	880	9.5	4.10	91.8	51.2
SB2	60	1.90	1.74	4220	760	4.85	1.88	92.7	72.3
SB3	240	3.81	3.37	2710	820	7.6	3.54	89.1	52.6
SB4	10	1.97	1.82	3930	820	4.5	1.93	92.1	62.1
SB5A	90	1.04	0.95	625	1600	43.5	1.07	88.8	84.1[d], 34.7[e]
SB5B	90	1.04	0.95	625	1600	11.7[c]	1.06	90.6	87.6[d], 73.5[e]
SB6	12	2.48	1.55	4330	590	3.0	1.63	61.7	55.2
SB7	100	0.84	0.78	2100	1000	15.5	0.85	89.6	55.3
SB12	15	0.32	0.29	2170	870	7.5	0.25	90.8	36.0
Optimum cure at 134.5° C									
SB8	45	1.42	0.90	4590	690	5.9	0.96	61.1	62.5
SB9A	15	0.88	0.78	2830	860	9.8	0.84	88.6	64.2
SB9B	30	1.66	1.47	4230	790	8.1	1.55	87.2	62.0
SB9C	1020	3.12	2.76	2750	680	6.1	2.94	75.6	23.8
SB10	100	0.57	0.52	410	1280	42.5	0.71	91.5	77.5
SB11	160	1.85	1.20	2940	570	12.7	1.31	59.4	74.0

[a] Iodine number of pure rubber, 372.8; of GR-S (23.4% styrene–76.6% butadiene), 359.5.
[b] After CH_3I treatment at 24° C. [c] Acetone only.
[d] Insoluble. [e] Soluble.

the acetone-chloroform-extracted stock had been treated with methyl iodide under nitrogen for the required time and the weight gain in the reaction ascertained, the rubber was removed and acetone-extracted. After drying at 60° C under 2 mm. of mercury pressure for 2 hours, total sulfur, iodine, unsaturation, and (where necessary) mercury and silver were determined. The recipes of

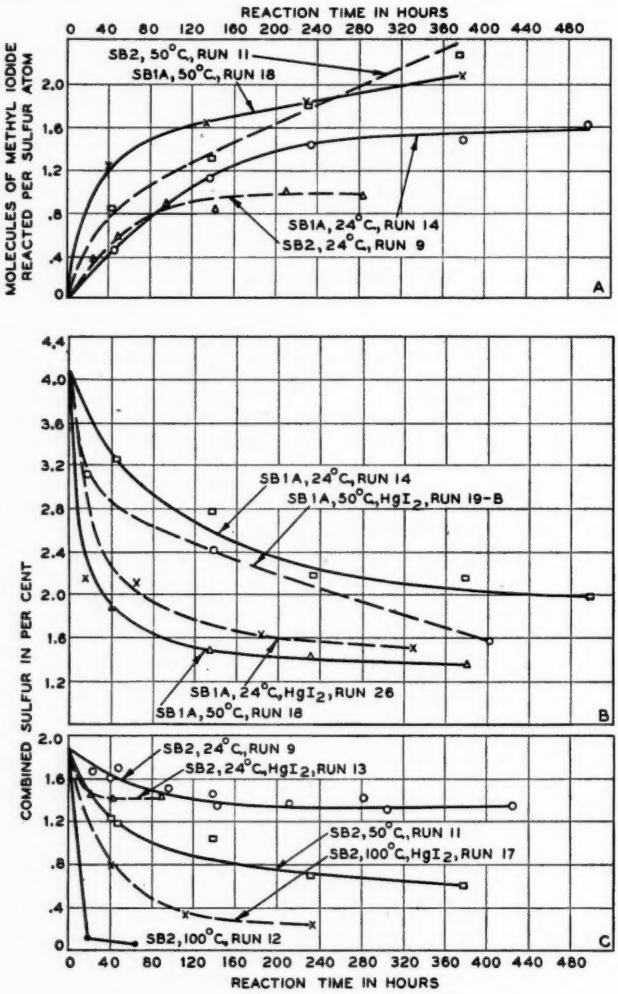

REACTION TIME IN HOURS
0 40 80 120 160 200 240 280 320 360 400 440 480
MOLECULES OF METHYL IODIDE REACTED PER SULFUR ATOM
SB2, 50°C, RUN 11
SB1A, 50°C, RUN 18
SB1A, 24°C, RUN 14
SB2, 24°C, RUN 9
A
COMBINED SULFUR IN PER CENT
SB1A, 24°C, RUN 14
SB1A, 50°C, HgI2, RUN 19-B
SB1A, 24°C, HgI2, RUN 26
SB1A, 50°C, RUN 18
B
SB2, 24°C, RUN 9
SB2, 24°C, HgI2, RUN 13
SB2, 50°C, RUN 11
SB2, 100°C, HgI2, RUN 17
SB2, 100°C, RUN 12
C
REACTION TIME IN HOURS

FIG. 1.—Reaction of methyl iodide with SB1A and SB2.

the stocks tested are given in Table I; the physical and chemical characteristics, in Table II.

Runs on GR-S gum stock SB5 were made on acetone-extracted (SB5B) and on acetone-chloroform-extracted (SB5A) stocks. In the latter case 43.5% was soluble. When either SB5A or SB5B was treated with methyl iodide, a part of the stock always dissolved in the reagent as the reaction progressed. This

part, called "soluble", was recovered by filtering the methyl iodide solution and evaporating off the reagent. Both the soluble and insoluble parts were then acetone-extracted, dried, and analyzed. At 24° C, about 33% of SB5B

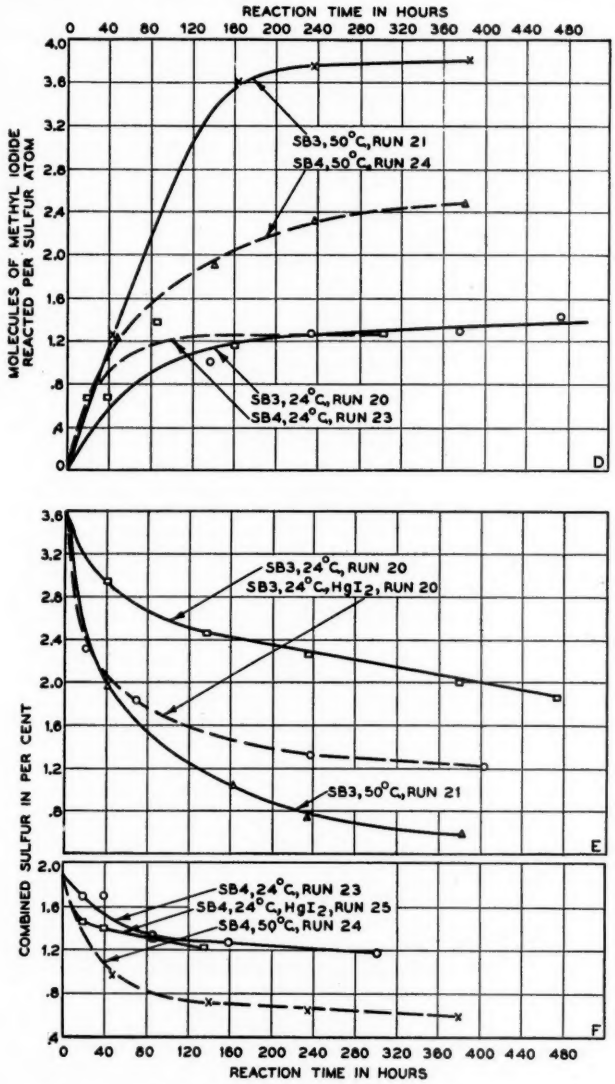

REACTION TIME IN HOURS
0 40 80 120 160 200 240 280 320 360 400 440 480
MOLECULES OF METHYL IODIDE REACTED PER SULFUR ATOM
SB3, 50°C, RUN 21
SB4, 50°C, RUN 24
SB3, 24°C, RUN 20
SB4, 24°C, RUN 23
D
COMBINED SULFUR IN PER CENT
SB3, 24°C, RUN 20
SB3, 24°C, HgI2, RUN 20
SB3, 50°C, RUN 21
E
SB4, 24°C, RUN 23
SB4, 24°C, HgI2, RUN 25
SB4, 50°C, RUN 24
F
REACTION TIME IN HOURS

FIG. 2.—Reaction of methyl iodide with SB3 and SB4.

was soluble in methyl iodide within 24 hours. This increased but little with time. The other GR-S gum stock, SB10, was about 20% soluble. With all the remaining stocks except SB7, the solubility after 500 hours at 24° C was only 2–3%. SB7, however, showed a solubility of 10%. In general, the sulfur content of the soluble portion, *i.e.*, that part of the dispersed rubber

which passed through coarse filter paper, was only 0.1–0.2% lower than that of the insoluble portion.

REMOVAL OF COMBINED SULFUR BY METHYL IODIDE

The combined sulfur of the acetone-extracted residue from the methyl iodide treatment is plotted against the reaction time for all stocks except SB7 and SB8 in Figures 1*B*, *C*; 2*E*, *F*; 3*H*, *I*, *J*; 4*K*, *L*, *M*; and 5. Since the sulfur elimination curves of SB7 and SB8 show no new features, they are not given. After 500 hours of reaction at 24° C, SB7 retains 0.47% combined sulfur and SB8 retains 0.60%. Figures 1*A*, 2*D*, and 3*G* show the quantity of methyl iodide reacting with the rubber, calculated on the basis of molecules of methyl iodide added for each sulfur atom originally combined in the rubber. It will be recalled that, for the sulfide type of linkage in which the sulfur is linked to an unsaturated residue, the two original carbon-sulfur bonds break, and the limit of addition is therefore 3 molecules of methyl iodide for each sulfur atom so combined (Equation 12 in Part I). The methyl iodide addition data are derived from the weight gain of the reaction flask contents after evaporation of

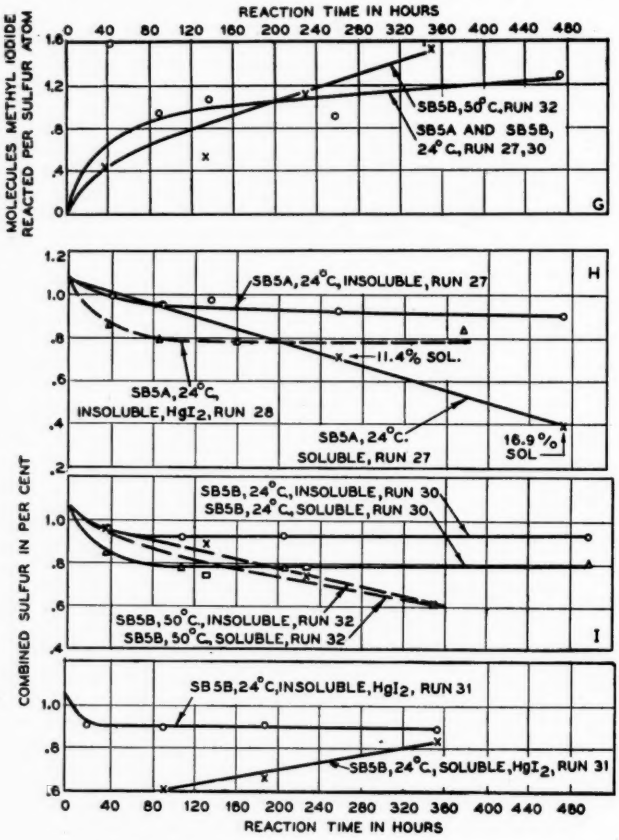

REACTION TIME IN HOURS
MOLECULES METHYL IODIDE REACTED PER SULFUR ATOM
SB5B, 50°C, RUN 32
SB5A AND SB5B, 24°C, RUN 27, 30
G
SB5A, 24°C, INSOLUBLE, RUN 27
11.4% SOL.
SB5A, 24°C, INSOLUBLE, HgI2, RUN 28
SB5A, 24°C. SOLUBLE, RUN 27
18.9% SOL
H
COMBINED SULFUR IN PER CENT
SB5B, 24°C, INSOLUBLE, RUN 30
SB5B, 24°C, SOLUBLE, RUN 30
SB5B, 50°C, INSOLUBLE, RUN 32
SB5B, 50°C, SOLUBLE, RUN 32
I
SB5B, 24°C, INSOLUBLE, HgI2, RUN 31
SB5B, 24°C, SOLUBLE, HgI2, RUN 31
REACTION TIME IN HOURS

FIG. 3.—Reaction of methyl iodide with SB5A and SB5B.

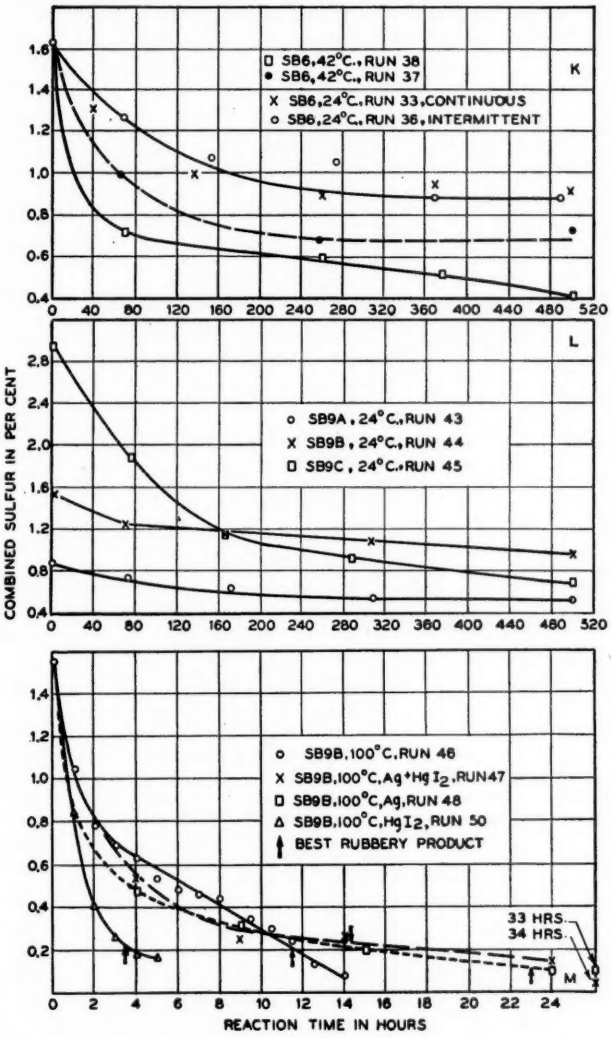

□ SB6, 42°C., RUN 38
• SB6, 42°C., RUN 37
X SB6, 24°C., RUN 33, CONTINUOUS
o SB6, 24°C., RUN 36, INTERMITTENT
K
o SB9A, 24°C., RUN 43
X SB9B, 24°C., RUN 44
□ SB9C, 24°C., RUN 45
L
COMBINED SULFUR IN PER CENT
o SB9B, 100°C., RUN 46
X SB9B, 100°C., Ag+HgI2, RUN 47
□ SB9B, 100°C., Ag, RUN 48
Δ SB9B, 100°C., HgI2, RUN 50
BEST RUBBERY PRODUCT
33 HRS.
34 HRS.
M
REACTION TIME IN HOURS

FIG. 4.—Reaction of methyl iodide with SB6, SB9A, B, and C at 24° C and 100° C.

excess reagent. In Figure 6 the tensile strength of the optimum-cure vulcanizates is plotted against sulfur remaining after methyl iodide reaction at 24° C.

The mercuric-iodide-catalyzed reaction was also studied. In general, about twice the theoretical weight of mercuric iodide was used. This theoretical weight was derived by considering all the sulfur in the rubber to be disulfide and recalling that the methyl iodide-*n*-propyl disulfide reaction, catalyzed with mercuric iodide, requires 2 molecules of mercuric iodide for each disulfide molecule (Equation 22 in Part I). A brief qualitative description of the reactions of the stocks with methyl iodide is given in Table III. Certain stocks are not given because their behavior duplicates the types listed. Thus, at 24° C,

SB7 behaves very much like SB2; SB8 and SB11 like SB6; SB9A, SB9B, and SB12 like SB4 except for the formation of more crystals; SB10 like SB5B; and SB3 and SB9C like SB1A, although no hydrogen sulfide is produced with SB9C.

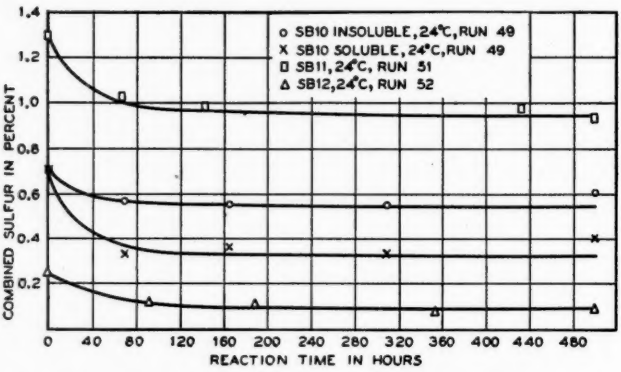


FIG. 5.—Reaction of methyl iodide with SB10, SB11, and SB12 at 24° C.

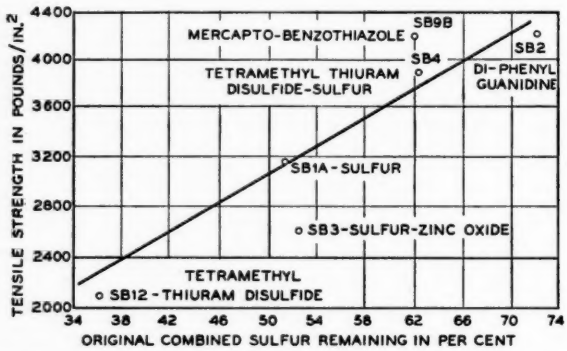


FIG. 6.—Tensile strength *vs.* sulfur remaining in optimum-cure vulcanizates after methyl iodide treatment at 24° C.

Disregarding for the present GR-S stock SB5, certain generalizations concerning the methyl iodide-vulcanizate reactions can be made from a study of the data in the tables and figures, which represent well over 500 experiments.

UNCATALYZED REACTION

In the rubber stocks studied, a part of the combined sulfur is removed as trimethylsulfonium iodide on reaction with methyl iodide at 24° C. In the case of the rubber-sulfur stock SB1A, a very small amount of free iodine is liberated at the same time. In some cases hydrogen sulfide is present.

The amount of combined sulfur removable at 24° C becomes nearly constant within 500 hours, except in the case of the rubber-sulfur-zinc oxide stock SB3. This value varies, with the vulcanizate, from 27.7 to 76.2% of the original combined sulfur (Table II, Figures 1 to 5).

In five of the rubber gum stocks investigated, *i.e.*, rubber-sulfur SB1A, diphenylguanidine-accelerated SB2, sulfur-tetramethylthiuram disulfide-acceler-

Table III

Color and Form Changes in Vulcanizate-Methyl Iodide Reaction

Run No.	Stock & catalyst	Temp., °C.	Description of reaction mixture[a]: Color of liquid[b]	H_2S odor	Crystals[c]	Color of rubber	Rubber particle	Acetone-extd. dried rubber: Color	Condition
14	SB1A	24	Yellow	Slight→strong	Few→many	Brown→darker	Swollen→very swollen	Yellow→brown	Soft, tacky
18	SB1A	50	Yellow	Strong	Many cubic	Brown-yellow	Very swollen→loss of shape	Orange→brown	Soft, elastic→stiff
26	SB1A & HgI_2	24	Wine red	None	Very few	Dark brown	Moderately swollen	Brownish	Hard
9	SB2	24	Colorless	...	No (Yes on evapn.)	Slightly yellow	Moderately swollen	Yellowish	No change from original; garlic smell
11	SB2	50	Colorless	Slight	Few→many	Brownish dirty	Moderately swollen	Biege	Not so elastic as run 9
12	SB2	100	Pink	Yes	...	...	Dissolved	Cream	Light powder
17	SB2 & HgI_2	50 40 hr.	Colorless	None	Some	Unchanged	Slightly swollen	Dirty yellow	Original shapes not hard
		100 hr.	Reddish	None	Many	...	Dissolved	Cream	Flakes like shellac
16	SB2 & Ag+HgI_2	100	Green-yellow	None	...	White-yellow	Undissolved→disintegration	Yellow	Sticky but with elasticity
23	SB4	24	Colorless	None→slight	Few	None→yellow	Slightly swollen	None→yellow	Soft, unchanged, slight garlic odor
24	SB4	50	Yellow	None	Few→many	Yellow→brown	Undissolved→partial soln.	Yellow→brown	Soft, tacky
25	SB4 & HgI_2	24	Colorless	None	Long needles	Yellow-white	Moderately swollen	Gray	Soft, tacky
27	SB5A	24	Colorless	None	None→few	None→yellow	Swollen 40 times →20% dissolved	Unchanged Yellowish	Insol. part like original Sol. part like pale crepe
28	SB5A & HgI_2	24	Colorless	None	None	Unchanged	Swollen more than run 27, some dissolved	Unchanged	Cohered in one thin sheet
32	SB5B	50	Yellow→red	...	Few→many	Yellow-orange	Very swollen→70% dissolved	Unchanged brown	Unchanged like crude GR-S
33	SB6	24	Colorless	No	Many	Unchanged	Slightly swollen, 2% sol.	Unchanged	Unchanged

[a] Arrow indicates increase, with reaction time, of the property, quality, or substance with which it is associated.
[b] When given as brown or red, free iodine is present.
[c] Crystals analyzed as trimethyl sulfonium iodide.

ated SB4, mercaptobenzothiazole-accelerated SB9B, and tetramethylthiuram disulfide-accelerated SB12—the percentage of sulfur remaining (referred to the originally combined sulfur of the stock) is proportional to the tensile strength for the optimum cure studied (Figure 6). Neither gum stocks SB3 and SB7, carbon-black-reinforced stocks SB6 and SB8, nor GR-S stocks SB5, SB10, and SB11 show this proportionality.

Careful study of the sulfur elimination curves of SB9A, SB9B, and SB9C shows that the sulfur which combined after the optimum period of cure is 100% removable by methyl iodide (Figure 4*L*). Further, during the overcure that part of the sulfur which is normally not removable by methyl iodide undergoes a chemical change so that part of it does react and splits out.

At 50° C the removal of sulfur is greater than at 24° C. After 400 hours of reaction, the sulfur remaining in stocks SB2, SB3, and SB4 is the same (0.6%). Physical changes, such as partial disintegration, are noticeable as increasing amounts of the combined sulfur are removed. In most cases free iodine and more hydrogen sulfide are liberated than at 24° C.

At 100° C, in the case of SB2 and SB9B, the combined sulfur may be almost completely removed, eventually producing a shellaclike thermoplastic material. On the other hand, the reaction of SB1A at 100° C for 185 hours does not remove any more sulfur than at 50° C. This is discussed in detail under "Catalyzed Reaction".

At 24° C, the amount of methyl iodide reacting with the vulcanizates is of the order of 1 molecule of methyl iodide for each atom of sulfur. When the temperature is raised to 50° C, between 2 and 3 molecules of methyl iodide react per sulfur atom.

Except for rubber-sulfur stock SB1A, there is no appreciable change in unsaturation at 24° C during removal of sulfur. The stock SB1A loses 5 to 10% of its unsaturation. At 50° C, however, there is a loss of around 30% in all but the tetramethylthiuram disulfide-accelerated stocks SB4, SB6, and SB12.

At 24° C, the iodine content of the reacted rubber after acetone extraction is 0.2 to 0.4% for all stocks except SB1A, which has 1.7% iodine. The iodine present, however, is only 3 to 10% of the value calculated on the assumption that 1 molecule of iodine remains combined in the rubber for each sulfur atom removed. The iodine content rises at 50° C, but still is only about half that calculated on the foregoing basis.

Experiments have shown that the level of sulfur remaining unreactive toward methyl iodide at 24° C, as established in these static experiments, is not lowered by alternate and repeated periods of reaction and extraction with acetone or by continuous refluxing of pure methyl iodide through the vulcanizate. No variations in reactant or product concentration, *i.e.*, mass law factors, affect the rate or extent of the methyl iodide-sulfur reaction at a given temperature.

CATALYZED REACTION

When mercuric iodide is used as a catalyst at 24° C, sulfur is eliminated down to the same level as in the uncatalyzed reaction in the case of SB2 and SB4. This level is reached in about one-third the time required for the uncatalyzed reaction. In the case of stocks SB1A and SB3, the sulfur is removed more quickly and, in addition, to a lower level than in the uncatalyzed reaction. Free iodine is present.

At 24° C with mercuric iodide, a loss of 20 to 30% in unsaturation is universal. At 24° C, the iodine and mercury contents of the treated rubber average from 0.2 to 2% and 2 to 5%, respectively, and are generally in the ratio 1.8 : 1 to 2.0 : 1. The actual ratio I_3 : Hg is 1.96.

At 50° C with SB2, the mercuric iodide reaction removes more sulfur than the uncatalyzed one; with SB1A less sulfur is removed. This last is an anomaly and may be due to a drastic change in the physical structure of the rubber (as evidenced by its hardness and brittleness), which would prevent the diffusion of methyl iodide to the sulfur links.

At 100° C, the use of a catalyst comprised of precipitated silver and mercuric iodide in the weight ratio of mercuric iodide to silver of 1 : 2 results in complete removal of sulfur from SB1A and SB2, with the production of an insoluble, rather elastic, and tacky material, in great contrast to the resin obtained from the uncatalyzed reaction.

The desulfurization of SB9B at 100° C with methyl iodide gives elastic products which look like undercured vulcanizates, with decreasing sulfur content down to 0.25% sulfur at 11 hours. After 11 hours of reaction the products are thermoplastic resins containing about 0.2% sulfur (Figure 4*M*).

The action of precipitated silver in the desulfurization of SB9B at 100° C is to delay resinification of the products from 11 to between 24 and 33 hours. The 24-hour product is an elastic rubber resembling milled pale crepe.

The mercuric iodide-catalyzed SB9B desulfurization is the fastest reaction. The best desulfurized rubber is obtained in only 3 hours. At 3.5 to 4 hours the transition to thermoplasts takes place.

The use of mercuric iodide plus silver in the above reaction with SB9B serves to accelerate the reaction only slightly. The transformation into resin, however, is inhibited. This inhibition is only temporary since, on heating to 100 hours, the product is resinous. The amorphous spacing of this resin, determined by x-rays, differs considerably from that of rubber. Fourteen-hour reaction gives a rubbery product with 0.2% sulfur.

Fifteen-gram batches of desulfurized SB9B were prepared by the four methods described above with the reaction times as indicated by the arrows in Figure 4*M*. These "reclaimed" products were compounded and vulcanized in the same manner as SB9B. The best reclaim stock was that made from the 3-hour mercuric iodide reaction. Hand tests indicated about 800–900 pounds per square inch at about 300% elongation. The other reclaim stocks had tensile strengths under 400 pounds per square inch but were fairly nervy.

GR-S STOCKS

Combined sulfur is present in the GR-S to the extent of 0.19%. Not only can this be reduced to 0.13% by treatment for 24 hours at 100° C with methyl iodide, but it can be eliminated entirely under the same conditions if mercuric iodide is present, with concomitant resinification of the rubber. All the figures given for sulfur content include this original 0.19%.

The insoluble portion of the diphenylguanidine-accelerated GR-S gum stock SB5B (recipe differs from SB2 only in the use of GR-S) behaves similarly to the pale crepe gum stock SB2 in regard to removal of sulfur at 24° C in the catalyzed and uncatalyzed reactions. The insoluble portion of SB5A resembles SB1A and SB3.

The soluble portion of SB5A increases in amount and decreases in sulfur content as the reaction progresses and is a direct result of it, since the vulcanizate had previously been acetone-chloroform-extracted, with removal of the

43.5% soluble material. The soluble portion of SB5B is constant in amount, and soon reaches a constant sulfur content like the insoluble portion of the stock; it does not differ from the latter in sulfur content at the start of the reaction, but it does differ by not having been sufficiently cross-linked to prevent solubility.

The mercaptobenzothiazole-accelerated GR-S gum stock SB10 behaves exactly as does SB5A. When, however, channel black is added to the compound as in SB11, the increase in tensile strength is accompanied by a sharp decrease in acetone-chloroform extract and almost negligible solubility in methyl iodide. A striking fact, moreover, is that the amount of methyl-iodide-removable sulfur is nearly the same in both the gum and reinforced stocks, *i.e.*, 22.5 and 26.0%, respectively. This same behavior holds true in the pale crepe gum stock SB9B and the channel black-reinforced SB8; 38.0 and 37.5% sulfur, respectively, is removed by methyl iodide at 24° C. This would indicate that the presence of reinforcing pigments does not change the chemical nature of the sulfur links which are sensitive to methyl iodide.

Vulcanized GR-S gum stocks are very soluble in solvents such as chloroform. The assumption is that, although sulfur is combined chemically in the proper linkages, the position of these links is not always such as to form continuous three-dimensional networks. The resulting small free volumes of the gel are then soluble; *i.e.*, they are removable from the net as colloidal particles.

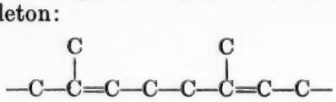
ACTION OF ALKALI AND THIOGLYCOLIC ACID

When acetone-chloroform-extracted SB9B is refluxed in alcoholic potassium hydroxide, the sulfur content is lowered from 1.55 to 1.32%. This alkali-removable sulfur has been explained by Kelly[36] as that sulfur which is combined with resins, proteins, or accelerators. After the SB9B has been reacted with methyl iodide at 24° C for 500 hours, it has 0.96% sulfur. If this material is then refluxed in alkali as above, the sulfur content drops to 0.58%. The greater amount of sulfur which is alkali removable in the methyl-iodide-reacted vulcanizate than in the unreacted SB9B could be due to removal of stable sulfonium compounds, in which the sulfur is linked to a paraffin residue as suggested by Geiger[37]. This will be treated in detail later.

Unlike its reducing action on the disulfide links of wool[38], thioglycolic acid in benzene solution apparently has no effect on rubber-sulfur stock SB1A or on a mercaptobenzothiazole-accelerated vulcanizate, such as SB9B. Samples of SB1A and SB9B, both fresh and reacted with methyl iodide, were immersed in 1 *M* thioglycolic acid for 200 hours at 24° C, extracted with benzene, and reacted 400 hours more with methyl iodide at 24° C. If any disulfide sulfur had been converted to mercaptan, the final sulfur content of the vulcanizate would have been lower than that obtained with just the methyl iodide treatment instead of being identical as they actually were. The thioglycolic acid was made 0.1 *M* with regard to hydroquinone to suppress addition of thioglycolic acid to the double bonds of the rubber[39].

DISCUSSION OF REACTIONS

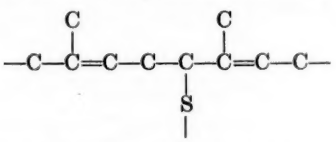
Three generally conceded premises must be allowed for the purposes of the discussion. First, the rubber hydrocarbon chain will be taken as a polyisoprene chain of the carbon skeleton:



(1)

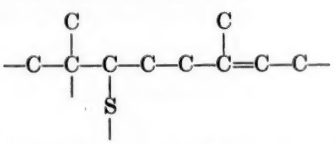
Secondly, the chemical reactions of such a chain, or of the sulfur attached to it, will differ from those of a simple dimer or trimer of isoprene only in overall rate, and this difference will be due in the main to purely physical phenomena such as diffusion and steric hindrance. The third premise is that, in all the extracted vulcanizates used in the methyl iodide reaction, no free sulfur is present.

It is convenient first to consider rubber-sulfur stock SB1A, rubber-sulfur-zinc oxide stock SB3, and the insoluble portion of GR-S gum stock SB5A in any attempt to relate the methyl iodide reaction data on vulcanizates to specific sulfur links. In these cases the mercuric iodide-catalyzed reaction not only is faster than the uncatalyzed, but removes more sulfur. However, with stocks SB2, SB4, and SB5 insoluble, the catalyzed reaction is merely faster but no more effective in removing combined sulfur. The behavior of all the vulcanizates at 24° C with methyl iodide parallels closely that of allyl sulfide. That is, part of the combined sulfur behaves as if it were attached to allyl residues. It is removed as trimethylsulfonium iodide, just as in the case of allyl sulfide (Equation 14 in Part I). Farmer showed that, in attacking the rubber chain, oxygen first forms a hydroperoxide on the carbon atom alpha to the double bond[40]. He also suggested the formation of the sulfur bridge in vulcanizates at an α-methylene carbon atom[41]. The active point of the polyisoprene chain, with regard to oxygen and probably sulfur, is the carbon atom alpha to the double bond. Any sulfur attached there as in:



(2)

would have, in effect, an allyl type residue on one of its two carbon linkages. On the other hand, if the sulfur bridge had in some way been formed at the double bond, thereby saturating it and giving:



(3)

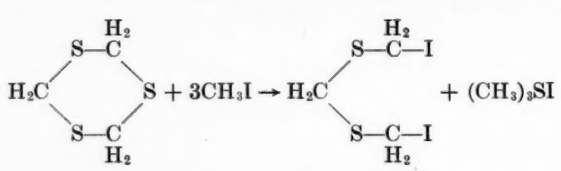
then one of the sulfur links on carbon would be a long-chain alkyl type residue, since the next double bond on the chain is 4 carbon atoms down the chain and probably does not influence the reactivity of the sulfur atom. Sulfides with such long-chain alkyl residues add methyl iodide to form stable sulfonium compounds[13] as shown by the good yields of the expected sulfonium salts (Equation 6 in Part I). Therefore, in all the vulcanizates the greater part of the sulfur which is removable at 24° C with methyl iodide is probably sulfide sulfur located at the carbon atom in alpha position to a double bond.

The small amounts of hydrogen sulfide also present in the SB1A reaction may result from a reaction of mercaptan links with methyl iodide to form hydrogen iodide and a sulfide, or by oxidation with iodine to form a disulfide and hydrogen iodide (Equation 2 in Part I), with the subsequent reaction of the hydrogen iodide produced with more mercaptan to produce hydrogen sulfide (Equation 5 in Part I). However, at 24° C it is unlikely that the latter reaction would be quantitative, especially in competition with the very fast

oxidation of mercaptan with iodine. In other words, if mercaptan is the source of the hydrogen sulfide, some hydrogen iodide could reasonably be expected. Since none was present, it is unlikely that the mercaptan linkage occurs to any large extent in the vulcanizates. The source of the hydrogen sulfide thus remains obscure.

The use of mercuric iodide in the reaction accelerates the removal of sulfur, which can be explained by referring to the catalytic action of the iodide on the reaction of simple sulfides with methyl iodide. However, since more sulfur is removed in the catalytic reaction than in the uncatalyzed one (for SB1A, SB3, and insoluble SB5A), disulfide sulfur may be present and react to give a sulfonium-mercuric iodide complex and free iodine (Equation 22 in Part I). The free iodine present at 24° and 50° C would support this. Where in the chain this disulfide sulfur is attached cannot be indicated as yet.

There remains, however, 36.6% of the original combined sulfur in SB1A which is not removed either in the catalyzed or uncatalyzed reactions. Even if the temperature is raised to 50° or 100° C in the uncatalyzed reaction with SB1A, it is impossible to remove the last 35% of the combined sulfur. It may be that some very stable sulfur linkage is present, such as a heterocyclic ring which does not react readily with methyl iodide. A second possibility is that the removal of part of the sulfur has changed the reactivity of the remaining sulfur links so as to render them unreactive. This is illustrated by considering the reaction of trithioformaldehyde with excess of methyl iodide at 100° C[42]:



(4)

Here the thioacetal formed does not react further with the methyl iodide, even at 100° C. This may be due to the iodine on the carbon atoms adjacent to the sulfur. An analogous situation might exist in the vulcanizate after removal of part of the sulfur. It is also possible that the apparently unreactive sulfur is the result of the effect of diminished concentration on the kinetics of the elimination reaction. Work is in progress to elucidate further the nature of this unreactive sulfur.

In accelerated stocks SB2 and SB4 and the insoluble portion of SB5B, the catalyzed reaction at 24° C removes no more sulfur than the uncatalyzed. Presumably either no disulfide linkages are present or the reaction is not carried to completion to split out all the sulfur. As with SB1A, SB3, and insoluble SB5A, a large amount of the sulfur is not removable at 24° C. But with all the stocks except SB1A, raising the temperature to 50° C removes considerably more sulfur than is removed at 24° C in the catalyzed reaction. With SB2 the uncatalyzed reaction at 100° C removes practically all the sulfur very quickly. There is thus some difference between sulfur links unreactive to methyl iodide at 24° C in rubber-sulfur stock SB1A and those in the accelerated stocks. Even the use of mercuric iodide at 100° C does not completely remove all the sulfur from SB1A. Only with silver and mercuric iodide can a sulfur-free product be obtained. Despite these differences, it can be said for SB1A, SB2, SB4, SB9B, and SB12 that the less sulfur that can be removed at 24° C with methyl iodide, the higher the tensile strength (Figure 6).

The inhibiting action of silver on the transformation from rubber to resin on desulfurization may be due to protection of the hydrocarbon from chain-splitting substitutive reactions by formation of silver iodide. On the other hand, the fact that, when silver is used as the catalyst, the rubber is not soluble until the transition to resin takes place can be explained as follows.

The net effect of the removal of sulfur, whether the original link was of any of the three classes, is the replacement of the carbon-sulfur link with a carbon-to-iodine bond (Equation 12 in Part I). In the course of the uncatalyzed reaction, this carbon-iodine bond is not stable. This is shown by the fact that, with SB1A at 24° C, only 11% of the calculated amount of iodine is found in the rubber (after acetone extraction) that would be present if one atom of sulfur was replaced by one iodine molecule, as is the case for the sulfide reaction. This is approximately doubled for the same sulfur content of the residue when the temperature is raised to 50° C. What happens to the free valence bond of the carbon when the carbon-iodine bond breaks is not known, but the unsaturation does not change except in the case of SB1A. However, when the silver-mercuric iodide catalyst is used, the resulting completely desulfurized material is largely insoluble in methyl iodide at 100° C and is, therefore, cross-linked. In addition, the amount of the material which remains soluble is directly proportional to the quantity of silver used. Evidently the iodine which has replaced the sulfur has, in turn, been removed by the silver. If a Wurtz type reaction occurred, the carbon atoms formerly attached to iodine would unit to form the required carbon-to-carbon cross link with formation of silver iodide. In effect, the carbon-sulfur link would be replaced by a carbon-carbon bond.

In all of the stocks treated with methyl iodide at 24° C, 0.2 to 0.4% iodine remains. This iodine could be combined as above or in the form of the stable sulfonium compounds, *i.e.*, where the sulfur is attached to paraffin residues. In this case Geiger[37] showed that in treatment with alkali the following reaction occurs:

$$-\overset{|}{\underset{|}{C}}-\overset{CH_3}{\overset{|}{\underset{I}{S}}}-CH_3 + KOH \rightarrow -\overset{|}{C}=CH_2 + (CH_3)_2S + HOH + KI \qquad (5)$$

Actually, the sulfur content of a sample of SB9B which had reacted with methyl iodide for 500 hours was only slightly reduced by treatment with alcoholic potassium hydroxide, but the iodine was removed completely.

Evidence as to whether the sulfur links in the vulcanizates are intra- or intermolecular is furnished by the solubility behavior of the vulcanizates during the reaction. It was shown above that the solution of vulcanized rubber cannot be brought about in the absence of oxygen when the solvent used does not attack sulfur links unless temperatures above 174° C are used. Since the methyl iodide reaction at 24° C was carried out in absence of oxygen, the solubility of the vulcanizate must be due to breaking of sulfur bonds. Since such solubility increases and results in completely soluble desulfurized products as the sulfur is removed in the absence of oxygen, a reasonably simple explanation is that the sulfur cross-links of a three-dimensional net are being broken, and that the resulting two-dimensional fragments are then soluble. This would indicate that the sulfur bonds responsible for vulcanization are intermolecular.

EXPERIMENTAL DETAILS

Preparation of rubber samples.—Pale crepe was taken from the same 25-pound portion of a bale of first grade crepe. A 10-pound portion of a 200-pound lot of GR-S with a low gel content served as a synthetic-rubber stock pile. The rubber chemicals were of the usual rubber trade standards. The compounds were mixed on a 6-inch laboratory mill, and were vulcanized immediately. The specimens were tensile-tested one hour after vulcanization. The sharpness and freedom from nicks of the dumbbell specimen cutter were found to be the most important factor in obtaining accurate tensile strength values.

Since the speed of reaction of methyl iodide with rubber is probably controlled to some extent by the surface available, it was desirable to have the rubber samples in finely divided form. The vulcanizates were first crumbed twice through tight, cold mill rolls. The thin crumbly sheets obtained were then cut into inch strips for subsequent chopping. Chopping was carried out with a modified Sunbeam meat chopper. Of the several types of chopper tried, this was the only one found satisfactory. It was modified by addition of a shielded ball-bearing race at the front end of the feed screw, with adjustment of the rear journal-type bearing surfaces so that no metallic chips would find their way into the rubber. This reduction procedure was satisfactory with all but stock SB5, which was undercured and somewhat tacky. The chopped rubber was then sifted in a nest of nickel-plated standard sieves. The particles which passed a 10- but not a 20-mesh sieve were used. All stocks were acetone-chloroform-extracted according to A.S.T.M. procedure[43]. The extracted rubber particles were dried at 60° C at 2 mm. mercury pressure for 3 hours. All the stocks, extracted or not, were stored in vacuum desiccators; the extracted stocks were evacuated to 0.01 mm. mercury pressure, and the others were kept under purified nitrogen. The samples were exposed to light as little as possible. Acetone extraction of the rubber after reaction was carried out according to A.S.T.M. procedure.

Apparatus and procedure.—The reaction of the vulcanizates with methyl iodide at 24° C was carried out essentially as described. The rubber, usually 0.2 to 0.4 gram, was weighed in a 125-cc., ground-joint Erlenmeyer flask. After addition of 57 grams (25 cc.) of purified methyl iodide and, where necessary, a weighed quantity of mercuric iodide or other catalyst, the stopcock assembly was attached and the whole put in place on the manifold (Figure 2 in Part I). Before freezing, the flask contents were pumped for about 30 seconds to free the rubber and solution from air. With the manifold stopcock just cracked and the pump going, the flask contents were gradually frozen. This had the effect of freeing the rubber and solution from the last traces of dissolved air given up as the liquid boiled at reduced pressure. Since, however, the temperature of the liquid was being lowered at the same time, not much methyl iodide was pumped out.

The subsequent rinsing with pure nitrogen, etc., was as described in Part I. After the completion of the reaction and subsequent weighing, the rubber was removed with tweezers and acetone-extracted. After drying at 60° C at 2 mm. mercury pressure, it was stored in weighing bottles in a vacuum desiccator at 0.01 mm. mercury pressure to await analysis.

When it was desired to work at 50° C, modified Erlenmeyer flask *D* (Figure 2 in Part I) was used. After addition of the rubber, the tube sealed to the flask was constricted to permit sealing under vacuum. When the reagents had been added and the boiling out, etc., completed, the flask was sealed off with the pump going. After the reaction was completed, the flask was frozen in

liquid air, the end of the flask tube broken off, and the flask sealed to a ground joint attached to the manifold. Glass blowing was done through a drying tube. The frozen flask was then evacuated, and the rest of the standard procedure carried out.

The modified Erlenmeyer flasks were satisfactory for work at 50° C *in vacuo* where the pressure was little more than 1 atmosphere, but when used at 100° C, they burst. The pressure of about 80–90 pounds per square inch at 100° C was successfully withstood by flask *E* (Figure 2 in Part I). This round flask had walls about 2.2 mm. thick. The same technique was used for sealing, etc., as for flask *D*. These flasks were placed in an oven at 100° ± 1° C in a loose-fitting steel bomb for safety. They were opened and sealed to a ground joint, as described for the modified Erlenmeyer flasks used at 50° C.

The reactions carried out at 24° C were placed in a constant-temperature room which varied ±1° C. Air ovens were used for the 50° and 100° C reactions. The temperature control was about ±1° C.

Analytical methods.—The combined sulfur of the unextracted stocks was determined by subtracting the free sulfur from the total sulfur. The free sulfur was determined by the sodium sulfite method[43] with the following modifications: The flasks, covered with watch glasses, are placed in an oven at 140° C for 2 hours. No paraffin is necessary. A hot plate at 140° C can be used instead if several grains of silicon carbide are added to each flask to prevent bumping. Although the solution boils at this temperature, frothing is negligible. When only nonsulfur-bearing accelerators are present, the rubber does not have to be separated from the sulfite solution before titrating.

In cases where enough sample was available, total sulfur was determined by the nitric acid wet-oxidation method recommended by the A.S.T.M.[43], using the procedure in which the zinc nitrate residue is baked to zinc oxide. Total sulfur was run on the methyl iodide-treated vulcanizates by a semimicro perchloric acid method. The sample weight taken was 50 mg. A modified semimicromethod similar to the A.S.T.M. nitric acid method was described by Luke[44]. The use of such small samples considerably reduces the danger of explosion in the perchloric acid method. A precision of about ±0.02% sulfur on the rubber is obtainable.

Where it was desired to obtain the sulfur analysis on the same day that the sample was prepared, a volumetric method developed by Luke[45] was used. This method involves oxidation of sulfur to sulfate by conventional procedures, reduction to sulfide with hydriodic acid, and titration of sulfide iodimetrically.

Iodine was determined by the Elek and Harte procedure[46], carried out in a Parr nickel microbomb. A 20-mg. sample was used. It is essential that the rubber be subdivided as finely as possible and well mixed with the fusion mixture.

The determination of mercury in the stocks which also contained combined iodine was carried out according to the method of Luke[44]. The rubber sample was oxidized by digestion with fuming sulfuric acid and potassium persulfate. Iodine was expelled by boiling with nitric acid. Finally the mercury was titrated by the Volhard method.

Silver was determined in the course of the total sulfur analysis. After the oxidation of the rubber, the silver was precipitated as the chloride, filtered off, converted to iodide, and weighed.

Unsaturation of natural rubber vulcanizates and GR-S stock was determined by the procedure of Kemp and Peters[47], using iodine chloride in carbon tetrachloride. This method is fairly satisfactory for GR-S vulcanizates but

does not give very accurate values for rubber vulcanizates. In this work, however, it was desired to follow only the changes in unsaturation during the methyl iodide reaction. The values obtained could be duplicated; and since the determinations were carried out in identical fashion on all samples of any given stock, it is felt that the results for the treated samples of any one stock are in the proper relation to one another.

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REFERENCES

[1] Brown and Hauser, *Ind. Eng. Chem.* **30**, 1291 (1938); RUBBER CHEM. TECH. **12**, 43 (1939); Hauser and Brown, *Ind. Eng. Chem.* **31**, 1225 (1939); RUBBER CHEM. TECH. **13**, 65 (1940).
[2] Thornhill and Smith, *Ind. Eng. Chem.* **34**, 218 (1942); RUBBER CHEM. TECH. **15**, 272 (1942).
[3] Farmer and Michael, *J. Chem. Soc.* **1942**, 513.
[4] Patterson, Geiger, Mizell and Harris, *J. Research Natl. Bur. Standards* **27**, 89 (1941); Harris, Mizell and Fourt, *J. Research Natl. Bur. Standards* **29**, 73 (1942); *Ind. Eng. Chem.* **34**, 833 (1942); Geiger, Division of Biological Chemistry, American Chemical Society meeting at Buffalo, Sept. 10–11, **1942**.
[5] Connor, in Gilman "Organic Chemistry—An Advanced Treatise", 2nd Ed., John Wiley & Sons, New York, **1943**, Vol. I, Chap. 10.
[6] Levine, Ph. D. thesis, University of Cincinnati, **1937**.
[7] Erdmann, *Ann.* **362**, 133 (1908).
[8] Weber, "Chemistry of India Rubber", Griffin & Co., London, **1902**, p. 92.
[9] Ingold and Jessup, *J. Chem. Soc.* **1930**, 713.
[10] Meyer and Hohenemser, *Helv. Chim. Acta* **18**, 1061 (1935); RUBBER CHEM. TECH. **9**, 201 (1936).
[11] Cahours, *Ann.* **135**, 354 (1865).
[12] Brown and Hauser, *Ind. Eng. Chem.* **30**, 1291 (1938); RUBBER CHEM. TECH. **12**, 43 (1939).
[13] Bost and Everett, *J. Am. Chem. Soc.* **62**, 1752 (1940).
[14] Bost and Conn, *Ind. Eng. Chem.* **23**, 93 (1931); **25**, 526 (1933).
[15] RÂy and Adhikari, *J. Indian Chem. Soc.* **7**, 297 (1930); Ray, *J. Indian Chem. Soc.* **8**, 537 (1931); Ray, Adhikari and Banerjee, *J. Indian Chem. Soc.* **8**, 739 (1931).
[16] RÂy and Adhikari, *J. Indian Chem. Soc.* **7**, 297 (1930).
[17] Ray and Levine, *J. Org. Chem.* **2**, 267 (1937).
[18] Backer and Stedehouder, *Rev. trav. chim.* **52**, 438 (1933).
[19] Hilditch and Smiles, *J. Chem. Soc.* **91**, 1394 (1907).
[20] Steinkopf and Müller, *Ber.* **56B**, 1926 (1923).
[21] Haas and Dougherty, *J. Am. Chem. Soc.* **62**, 1004 (1940).
[22] Ellis and Reid, *J. Am. Chem. Soc.* **54**, 1674 (1932).
[23] Ayers and Agruss, *J. Am. Chem. Soc.* **61**, 83 (1939).
[24] Banerjee, *Z. anorg. allgem. Chem.* **83**, 113 (1913).
[25] Bezzi, *Gazz. chim. ital.* **65**, 693 (1935).
[26] Smyth and McAlpine, *J. Chem. Physics* **2**, 1499 (1934).
[27] Kimball, Kramer and Reid, *J. Am. Chem. Soc.* **43**, 1199 (1921).
[28] Van Rossem, *India-Rubber J.* **92**, 845 (1936); RUBBER CHEM. TECH. **10**, 203 (1937); Brown and Hauser, *Ind. Eng. Chem.* **30**, 1291 (1938); RUBBER CHEM. TECH. **12**, 43 (1939); Hauser and Brown, *Ind. Eng. Chem.* **31**, 1225 (1939); RUBBER CHEM. TECH. **13**, 65 (1940); Fisher, *Ind. Eng. Chem.* **31**, 1381 (1939); RUBBER CHEM. TECH. **13**, 50 (1940); Hauser and Smith, *India Rubber World* **101**, No. 2, 31 (1939); RUBBER CHEM. TECH. **13**, 243 (1940); Busse, *Ind. Eng. Chem.* **31**, 1391 (1939); RUBBER CHEM. TECH. **13**, 196 (1940); Booth and Beaver, *Ind. Eng. Chem.* **32**, 1006 (1940); RUBBER CHEM. TECH. **13**, 918 (1940); Hauser and Sze, *J. Phys. Chem.* **46**, 118 (1942); RUBBER CHEM. TECH. **15**, 560 (1942); Tobolsky, *J. Chem. Physics* **11**, 290 (1943).
[29] Williams, *Ind. Eng. Chem.* **26**, 1190 (1934); RUBBER CHEM. TECH. **8**, 102 (1935); *Proc. Rubber Tech. Conf. London*, **1938**, 304; RUBBER CHEM. TECH. **12**, 191 (1939).
[30] Williams, *Proc. Rubber Tech. Conf. London*, **1938**, 304; RUBBER CHEM. TECH. **12**, 191 (1939); Stock No. 4.
[31] Williams, *Ind. Eng. Chem.* **26**, 1190 (1934); RUBBER CHEM. TECH. **8**, 102 (1935).
[32] Kemp and Mueller, *Ind. Eng. Chem. Anal. Ed.* **6**, 52 (1934); RUBBER CHEM. TECH. **7**, 576 (1934); Blake and Bruce, *Ind. Eng. Chem.* **29**, 866, (1937); RUBBER CHEM. TECH. **10**, 735 (1937).
[33] Tobolsky, *J. Chem. Physics* **11**, 290 (1943).
[34] Smith and Taylor, *J. Research Natl. Bur. Standards* **13**, 463 (1934); RUBBER CHEM. TECH. **8**, 214 (1935); Kemp and Peters, *J. Phys. Chem.* **43**, 923 (1939); RUBBER CHEM. TECH. **13**, 28 (1940).
[35] Smallwood (U. S. Rubber Co.), British patent 533,669 (Feb. 18, 1941); Canadian patent 403,992 (Apr. **7**, 1942).
[36] Kelly, *Ind. Eng. Chem.* **12**, 875 (1920); **14**, 196 (1922).
[37] Geiger, Division of Biological Chemistry, American Chem. Soc. meeting at Buffalo, Sept. 10–11, **1942**.
[38] Patterson, Geiger, Mizell and Harris, *J. Research Natl. Bur. Standards* **27**, 89 (1941).
[39] Karasch, Read and Mayo, *Chemistry & Industry* **57**, 752 (1938).
[40] Farmer, *Trans. Faraday Soc.* **38**, 340 (1942); RUBBER CHEM. TECH. **15**, 765 (1942); Farmer, Bloomfield, Sundralingam and Sutton, *Trans. Faraday Soc.* **38**, 348 (1942); RUBBER CHEM. TECH. **15**, 756 (1942); Farmer and Sundralingam, *J. Chem. Soc.* **1942**, 121; RUBBER CHEM. TECH. **16**, 17 (1943); Farmer and Sutton, *J. Chem. Soc.* **1942**, 116, 139; RUBBER CHEM. TECH. **16**, 45 (1943).
[41] Farmer, *Trans. Faraday Soc.* **38**, 356 (1942); RUBBER CHEM. TECH. **15**, 774 (1942); Farmer and Michael, *J. Chem. Soc.* **1942**, 513.
[42] Reychler, *Bull. Soc. chim.* [3] **33**, 1226 (1905).
[43] Am. Soc. Testing Materials, "Standards on Rubber Products", **1941**, p. 1.
[44] Luke, *Ind. Eng. Chem. Anal. Ed.* **15**, 597 (1943).
[45] Luke, *Ind. Eng. Chem. Anal. Ed.* **15**, 602 (1943).
[46] Elek and Harte, *Ind. Eng. Chem. Anal. Ed.* **9**, 502 (1937).
[47] Kemp and Peters, *Ind. Eng. Chem. Anal. Ed.* **15**, 453 (1943).

MACROMOLECULAR COMPOUNDS. CCXCII

POLYISOBUTYLENE *

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INTRODUCTION

An explanation of the chemical constitution of macromolecular substances has to a great extent been made possible by the preparation and study of various homologous series of polymers[4]. In these investigations, the relations between the average degrees of polymerization and the physical properties of the particular substances concerned were studied. As a result of these studies, it was found that the unusual physical properties of macromolecular substances, such as toughness, elasticity, swelling in liquids, and above all, the colloidal nature of their solutions, are dependent on the size and form of their macromolecules, and not on a special micellar structure, as had been so widely assumed previously[3].

It has been found possible to prepare a complete series of homologous polymers, starting with the low members, and passing through the hemicolloids and mesocolloids, to the highest molecular members, the eucolloids[4], by polymerization of vinyl derivatives under various conditions[2]. It has not been found possible, however, to prepare a complete series of homologous polymers from all vinyl derivatives. At present, for example, there are still no known eucolloid members of polyindenes[5] and of polyanetholes[6]. On the other hand, in the polymerization of styrene[7], vinyl chloride, acrylic esters and vinyl acetate, it has been found possible to prepare, by the proper choice of conditions during polymerization, members extending from hemicolloids to eucolloids. An analogous complete series of homologous polymers can be prepared from polyisobutylenes. In this case it is possible, by the choice of various catalysts, to obtain polymerized products extending from the lowest to the highest degrees of polymerization. The hemicolloid members of this series are used technically as lubricating oils[8]; the mesocolloid and eucolloid products are of importance in other ways because of their rubberlike properties[9].

PREPARATION OF POLYISOBUTYLENES

The polymerization of isobutylene has been the subject of numerous investigations, and the patent literature is particularly extensive in this respect. Relatively low-molecular, distillable products with degrees of polymerization of 3 to 12 have been prepared by Lebedev and Filonenko[10] by the action of floridine on isobutylene, and by Waterman[11] by the use of aluminum chloride and silica gel. Staudinger and Brunner[14] were able to isolate a hemicolloidal product having an average degree of polymerization of 27.

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To obtain larger quantities of hemicolloidal products, the present authors polymerized isobutylene (160 grams) with dehydrated Florida earth (150 grams), and separated the low-molecular, distillable products (approximately 100 grams) by treatment with acetone. The low-molecular, acetone-soluble components were separated by distillation in a vacuum and finally in a high vacuum, and in this way liquid polyisobutylenes of an average degree of polymerization of 3–12 were obtained. These were not, however, examined further. The acetone-insoluble, hemicolloidal members were separated into relatively high-molecular and low-molecular fractions by fractional precipitation from benzene solution by acetone. The low-molecular components were separated from the high-molecular components also by extraction with hot acetone.

Mesocolloidal and eucolloidal polyisobutylenes having average degrees of polymerization over 500 can be obtained by polymerization with boron fluoride, according to the process of Hofmann[13]. At ordinary temperatures, polymerization proceeds energetically, and mesocolloidal products are formed. On the other hand, at −80° C polymerization is slow, and eucolloidal products are obtained[14]. Hence in this case too, the same phenomena are involved as in other similar polymerization processes, *e.g.*, in the polymerization of styrene[15], that is, at low temperatures the products are of higher average degrees of polymerization than those which are formed at higher temperatures[16].

In addition, a series of technical products was available[17] for the experiments to be described. These mesocolloidal and eucolloidal polymers were separated into their individual fractions by solution in toluene and fractional precipitation by acetone or methanol. They were then purified by repeating these operations.

Some of these polymers were analyzed, and were found to have the general composition, $(CH_2)_n$.

TABLE 1

ANALYSES OF MESOCOLLOIDAL AND EUCOLLOIDAL POLYISOBUTYLENES[18]

Product	Fraction	$\bar{P}$	C (percentage)	H (percentage)	Ash
Polyisobutylene I	1	9,000	85.73	14.47	——
	2	4,500	86.05	14.17	——
Polyisobutylene II	1	1,600	85.71	14.46	——
	2	1,100	85.74	14.30	——
	3	600	85.70	14.30	——
Calculated for $(C_4H_8)_x$			85.63	14.37	

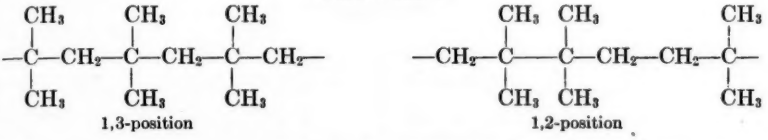
With respect to the formation of low-molecular polymers which are products of the action of floridine or of aluminum chloride on isobutylene, these polymers are probably formed by a condensation type of polymerization[19], whereby a monomeric molecule unites at the double bond of another molecule after migration of a hydrogen atom. The double bond of the dimeric product can then react with another monomeric molecule, and so on progressively.

Only products of relatively low degrees of polymerization are formed by a condensation polymerization of this character, since the double bond is relatively inactive in products of relatively high molecular weights. Mesocolloidal and eucolloidal products owe their formation to chain reactions[20], which in the case concerned in the present work have not been studied.

To explain the constitution of these polymeric products, it would be necessary to determine whether the monomeric molecules unite with one another

in such a manner that their methyl groups are always in the 1,3-position or in the 1,2-position, or whether both arrangements are present in the polymeric molecules.

STRUCTURE 1



This question has not yet been finally settled[21]. Since, however, these substituents are located in 1,3-position in polystyrenes[22] and in polyvinyl acetates[23], it may rightfully be assumed that this is true also of polyisobutylenes[24].

It must be ascertained further whether fibre molecules are formed by the polymerization of isobutylene, or whether the macromolecules of polyisobutylene are long, yet at the same time are branched. The formation of such irregularly constructed macromolecules may be attributable to small percentages of impurities[25] in the starting material[26], which may induce reactions which lead to branching. Such impurities are not at all impossible in technical isobutylene.

Finally an investigation must be carried out to ascertain what end groups are present on the polyisobutylene chain; *e.g.*, one end group might be a methyl group and the other end group an ethylene bond. This question might possibly be answered by a study of the hemicolloidal members of the series.

The investigation now to be described is concerned chiefly with the determination of the degrees of polymerization of polyisobutylenes, with a view to throwing light on the relations between chain length and physical properties.

RELATION BETWEEN THE PHYSICAL PROPERTIES AND CHAIN LENGTH OF POLYISOBUTYLENES

The same relations between physcal properties and average degree of, polymerization hold true of polyisobutylenes as are true of hydrorubbers of similar structure[27]. In the case of hydrorubbers the eucolloidal members are, to be sure, not easily prepared, so they have not been studied very thoroughly up to the present time, whereas the eucolloidal members of the polyisobutylene series are readily prepared. The changes in physical properties with increase in the degree of polymerization are evident from the data presented in Table 2.

The low-molecular polyisobutylenes up to a degree of polymerization of 12 are liquids which can be distilled, and the viscosities of which increase with increase in molecular weight. The hemicolloidal products with degrees of polymerization from 20 to 150 are tough, sticky masses of the same general character as hemicolloidal rubbers and hydrorubbers. Their high degree of tackiness is unexpected, and this increases to a degree of polymerization of about 50, above which it decreases and is no longer appreciable in mesocolloidal products and especially in eucolloidal products. Mescolloids, especially eucolloidal polyisobutylenes, are elastic, and resemble natural rubber and eucolloidal rubber. As has already been shown by studies of eucolloidal hydrorubber, the double bonds are probably not responsible for the elastic properties of rubber, as has been believed in the past[28]; instead, the elasticity of this hydrocarbon is a function only of the length of the molecules[29], for rubbers, hydro-

TABLE 2

CHANGES IN PHYSICAL PROPERTIES OF POLYISOBUTYLENES WITH INCREASE IN THE AVERAGE DEGREE OF POLYMERIZATION

Product	Average degree of Polymerization	Properties	Solubility and tendency to swell						
			Acetone	Ether	Benzene	Cyclo-hexane	Carbon Tetrachloride	Tendency to swell	Viscosity of a 1% solution*
Low molecular-weight substances	5–12	distillable oil	soluble	easily soluble	easily soluble	easily soluble	easily soluble	rapid solution without swelling	sol solutions of very low viscosity
Hemicolloids	20–150	sticky, viscous masses	not soluble	soluble	easily soluble	easily soluble	easily soluble	soluble without swelling	sol solutions of low viscosity
Mesocolloids	150–2000	plastic and elastic masses	not soluble	difficultly soluble	soluble	easily soluble	easily soluble	soluble with moderate swelling	viscous gel solutions
Eucolloids	2000–5000	tough, slightly plastic, highly elastic masses	not soluble	not soluble	difficultly soluble	soluble	soluble	slowly soluble with much swelling	highly viscous gel solutions

* For reference to sol and gel solutions, see Staudinger, "Organische Kolloidchemie", 2nd Ed., Verlag Vieweg, Braunschweig, 1941, p. 78.

rubbers and polyisobutylenes having about 3000–5000 atoms in their chains have approximately the same elasticity[30]. It has been shown further that, in this group of high polymeric hydrocarbons, plasticity decreases with increase in the degree of polymerization, whereas elasticity increases[31].

Kuhn[32], Meyer, Mark and others have assumed that, during elastic extension, the strongly kinked macromolecules present in the unstretched hydrocarbons are straightened out. The crystallization which results from stretching such highly polymeric hydrocarbons is readily explained in this way. Likewise mesocolloidal and eucolloidal polyisobutylenes crystallize readily when they are stretched[33]. This supports the view that long, straight, unbranched molecular chains are present in these hydrocarbons.

This theory of elasticity and crystallization which is now so widely accepted, is at variance with a series of observations which support the idea that organic molecules have a stable form[34]. For example, viscosity measurements indicate that the macromolecules of linear macromolecular substances have in solution essentially the same elongated form that they do in the solid state[35]. If such a conclusion is correct, the elasticity and crystallization of high polymeric hydrocarbons must be explained in some other way. Only then is it possible to answer the question whether further light is thrown on the problem of the form of the macromolecules of these high-polymeric hydrocarbons, both in solution and in the solid unstretched state. Above all else, the constitution of these hydrocarbons must be explained, for it has not yet been demonstrated conclusively whether or not long, straight macromolecules, not only of rubber and hydrorubber[36] but also of polyisobutylenes, are branched[37].

With respect to the solubility of the various members of homologous polyisobutylenes, the same general facts hold true which are true of other polymeric homologs. Members with relatively low molecular weights are easily soluble in a large number of organic solvents or are miscible with them. With increase in molecular weight, the solubility decreases, and products with the highest molecular weights are soluble in only a limited number of solvents, in fact only in those which have a particularly strong solvating action on the dissolved macromolecules[38]. For example, mesocolloidal polyisobutylenes and eucolloidal polyisobutylenes are much more readily soluble in cyclohexane than in benzene. That aliphatic cyclohexane solvates polyisobutylenes more strongly than does aromatic benzene is evident from the fact that the viscosity constants of polyisobutylenes are higher in cyclohexane than in benzene. This is the case of hydrorubber as well, and general experience has proved that the more a substance is solvated by a solvent, the higher is the viscosity constant of the substance in the solvent[39].

Differences in the solubility of high-molecular substances in different solvents can be shown very easily by measuring the quantity of precipitating agent which must be added to a solution to bring about precipitation. This proportion is much greater in good solvents than in poor solvents[39].

According to the data in Table 3, cyclohexane is the best solvent for polyisobutylenes, since the greatest proportion of precipitant is required to precipitate the polymeric hydrocarbon from its solution. Benzene is the poorest solvent, for in this case only relatively small proportions of precipitant are required to bring about precipitation. Toluene is a better solvent than purely aromatic benzene for polyisobutylenes, probably because of its aliphatic methyl groups. The more highly polymerized substances are more difficultly soluble in all solvents than are polymers of lower molecular weights[40].

At the beginning of the work, the object of which was to explain the constitutions of rubber and of hydrorubber, the surprising fact was discovered that substances having molecular weights in the range from 100,000 to 500,000 are still readily soluble in organic solvents, particularly in view of the fact that such a compound as hexacontane, with a molecular weight of 842, is difficultly soluble in organic solvents, and paraffins of still higher molecular weights,

TABLE 3

SOLUBILITY OF EUCOLLOIDAL POLYISOBUTYLENES IN VARIOUS SOLVENTS

(c = 5 g. per liter)

$$\text{Solubility} = \frac{\text{moles of precipitant}}{\text{moles of solvent}}$$

Solvent	Average degree of polymerization 1200		Average degree of polymerization 1700		Average degree of polymerization 2600	
	Precipitated by acetone	Precipitated by methanol	Precipitated by acetone	Precipitated by methanol	Precipitated by acetone	Precipitated by methanol
Cyclohexane	1.52	*	1.11	*	0.97	*
Carbon tetrachloride	0.71	0.56	0.51	0.38	0.47	0.36
Hexane	0.68	*	0.60	*	0.59	*
Benzene	0.24	0.28	0.09	0.11	0.02	0.05

* Methanol is not miscible with cyclohexane or with hexane, and therefore cannot be used as a precipitating agent in these cases.

i.e., of 5000 or greater, dissolve in organic solvents only when heated[41]. The ready solubility of polyisobutylenes depends on their stable, lateral methyl groups[44].

By transforming polyprenes into polymerically analogous polypranes, it was proved that the colloidal particles in their solutions are macromolecules[43], not micelles, as had been believed previously[44]. In the case of polyisobutylenes, no such direct proof of a macromolecular structure of the colloidal particles has yet been offered, since it has not been found possible to transform these relatively inactive hydrocarbons into polymerically analogous products. Since, however, in the homologous series of polyisobutylenes, the relations between the physical properties of the individual members and the size of the colloidal particles are similar to those which hold true of rubber, a macromolecular structure of the colloidal particles in solutions of eucolloidal polyisobutylenes may be assumed[45]. Obviously this holds true only of solutions in good solvents. Solutions of eucolloidal polyisobutylenes in benzene behave abnormally in many respects, and therefore it cannot be proved without further investigation whether or not the colloidal particles in such solutions consist of associations or macromolecules[46].

As with other linear macromolecular substances[47], the tendency of the individual members of the homologous polymeric series of polyisobutylenes to swell is a function of the length of their molecules. Hemicolloidal members are soluble without any tendency to swell; with increase in chain length swelling phenomena become evident, and eucolloidal polyisobutylenes having average degrees of polymerization of 2000–5000 dissolve in solvents, with accompanying marked swelling (see Table 2). This is in agreement with the fact that the sphere of action of long straight fibre molecules is so great that they have freedom of movement only in relatively dilute solutions. Solutions of eucolloidal polyisobutylenes which have been diluted to approximately 1 per cent

concentration are gel solutions; and only very dilute solutions, the specific viscosities of which are 0.2 or less, are sol solutions, with freedom of movement of the macromolecules. Solutions of eucolloidal polyisobutylenes show deviations from the Hagen-Poiseuille law, as is the case of all solutions of eucolloidal linear macromolecular substances[48].

APPLICATION OF THE VISCOSITY LAW TO HEMICOLLOIDAL POLYISOBUTYLENES

According to the viscosity law of linear macromolecular substances, the viscosity constant, $\lim_{c \to 0} \eta_{sp}/c = Z_\eta$, in sol solutions increases in proportion to the number of chain atoms (n) in the fibre molecules.

$$Z_\eta = K_m P = K_{equiv.}\, n. \tag{1}$$

The $K_{equiv.}$ value of low-molecular paraffins and their derivatives is 0.95×10^{-4} in benzene[49], 1.05×10^{-4} in carbon tetrachloride[49], and 1.2×10^{-4} in cyclohexane[50].

The viscosity constants of four hemicolloidal members in these three solvents were determined. These constants were lowest in benzene, the poorest solvent; and were highest in cyclohexane, the best solvent (see Table 4). At the same time the temperature effect was ascertained by determining the ratios between the viscosity constants Z_η at 60° to the viscosity constants Z_η at 20°. In cyclohexane and in carbon tetrachloride, the temperature effect was approximately the same as it was with hydrocarbons of low molecular weights. In benzene, on the contrary, the temperature effect was somewhat greater, possibly because in this solvent the molecules are associated to a slight extent.

TABLE 4

VISCOSITY MEASUREMENTS OF HEMICOLLOIDAL POLYISOBUTYLENES IN VARIOUS SOLVENTS

Solvent	Fraction	Average degree of polymerization	Concentration (g. per l.)	η_r (20° C)	Z (20° C)	η_r (60° C)	Z_η (60° C)	$\frac{Z_\eta \text{ at } 60°}{Z_\eta \text{ at } 20°}$
Cyclohexane	1	26	27	1.170	0.0063	1.140	0.0052	0.83
	2	39	20	1.172	0.0086	1.148	0.0074	0.86
	3	40	20	1.101	0.0096	1.167	0.0083	0.87
	4	59	16	1.235	0.0147	1.203	0.0127	0.87
Carbon tetrachloride	1	26	26	1.152	0.0058	1.127	0.0049	0.83
	2	39	20	1.159	0.0080	1.136	0.0068	0.85
	3	40	23	1.206	0.0090	1.177	0.0077	0.86
	4	59	15	1.196	0.0130	1.173	0.0115	0.89
Benzene	1	26	31	1.152	0.0049	1.141	0.0046	0.94
	3	39	28	1.188	0.0067	1.184	0.0066	0.99
	3	40	29	1.207	0.0071	1.212	0.0073	1.03
	4	59	14	1.137	0.0098	1.140	0.0100	1.02

The average molecular weights and the average degrees of polymerization of these four hemicolloidal products in cyclohexane were measured cryoscopically.

The data in Table 5 should be confirmed by molecular weight determinations in other solvents. In benzene, the poorest solvent for polyisobutylenes, somewhat higher molecular weights were obtained in all cases, a further indication

that association takes place. Cryoscopic molecular weight determinations of this kind should be judged with a certain degree of caution, however, because, with linear macromolecular substances, many abnormal freezing-point depressions have been observed, not only with polysaccharides [51] but also with polyanetholes[52].

TABLE 5

CRYOSCOPIC DETERMINATION OF HEMICOLLOIDAL POLYISOBUTYLENES IN CYCLOHEXANE

Fraction	Solvent (grams)	Substance (grams)	Δ	$\overline{M}$	$\overline{P}=\overline{M}/56$
1	27.2	0.3780	0.197	1420	25
	27.2	0.3744	0.193	1440	26
2	27.2	0.3191	0.108	2200	39
	27.2	0.3644	0.121	2200	39
3	27.2	0.3073	0.100	2300	41
	27.2	0.4881	0.170	2100	38
4	27.2	0.3073	0.065	3500	62
	27.2	0.3854	0.091	3100	55

The K_m constants were then calculated from the average degrees of polymerization and viscosity constants, and the $K_{equiv.}$ constants were calculated from the viscosity constants and number of chain-members (n), according to Equation (1) (see Table 6).

The calculated $K_{equiv.}$ constants of hemicolloidal polyisobutylenes have approximately the same values as those of low-molecular homogeneous compounds. This is evident in the data summarized in Table 7.

TABLE 6

DETERMINATION OF THE $K_{equiv.}$ CONSTANTS OF HEMICOLLOIDAL POLYISOBUTYLENES IN VARIOUS SOLVENTS

Solvent	Fraction	Average degree of polymerization	n	Z_η	$K_m \times 10^4$	$K_{equiv.} \times 10^4$
Cyclohexane	1	26	52	0.0063	2.4	1.2
	2	39	78	0.0086	2.2	1.1
	3	40	80	0.0096	2.4	1.2
	4	59	118	0.0147	2.4	1.2
Carbon tetrachloride	1	26	52	0.0058	2.2	1.1
	2	39	78	0.0080	2.0	1.0
	3	40	88	0.0090	2.2	1.1
	4	59	118	0.0130	2.2	1.1
Benzene	1	26	52	0.0049	1.9	0.94
	2	39	78	0.0067	1.7	0.86
	3	40	80	0.0071	1.8	0.89
	4	59	118	0.0098	1.7	0.83

TABLE 7

COMPARISON OF THE $K_{equiv.}$ CONSTANTS OF FRACTIONATED HEMICOLLOIDAL POLYISOBUTYLENES WITH THOSE OF LOW-MOLECULAR, HOMOGENEOUS SUBSTANCES

	$K_{equiv.}$ constant		
Product	in cyclohexane	in carbon tetrachloride	in benzene
Low-molecular, homogeneous substances	1.2×10^{-4}	1.05×10^{-4}	0.95×10^{-4}
Hemicolloidal polyisobutylenes	1.2×10^{-4}	1.08×10^{-4}	0.9×10^{-4}

According to the data in Table 7, the viscosity law holds true of hemicolloidal polyisobutylenes with 52 to 118 chain members. The lateral methyl groups have, therefore, no influence on viscosity. There are, accordingly, compounds with chains of equal length, *i.e.*, compounds analogous with respect to their chains, which have the same viscosity constants, independent of the diameters of their fibre molecules, assuming, of course, that compounds of different diameters are equally solvated[53]. The macromolecules of hemicolloidal polyisobutylenes are, therefore, constituted as shown in Formulas (1) and (2). Branchings resulting from side reactions are not present in these macromolecules.

RELATIONS BETWEEN VISCOSITY CONSTANTS AND AVERAGE DEGREES OF POLYMERIZATION OF MESOCOLLOIDAL AND EUCOLLOIDAL POLYMERS

THE VISCOSITY LAW WITH MESOCOLLOIDAL AND EUCOLLOIDAL POLYMERS

The patent literature contains much information concerning the degree of polymerization of these technically important products. The values given are presumably calculated from viscosity measurements, with the assumption that the viscosity law is applicable to mesocolloidal and eucolloidal polyisobutylenes, as it is to cellulose and cellulose derivatives[54]. Other investigations have shown, however, that, in the case of synthetic high polymers, especially polyvinyl derivatives, the relations are more complicated. Polystyrenes prepared at different temperatures are not polymerically analogous, because the higher the temperature at which polymerization is carried out, the smaller are the K_m constants of the polystyrenes. On the other hand, when polymerization is carried out at the same temperature, a mixture of homologous polystyrenes[55] (see Table 8) is obtained, and these have the same K_m constants, irrespective of whether the polystyrenes are obtained by polymerization of pure styrene or of styrene solutions. To explain these phenomena, it has been assumed that polystyrenes with different degrees of branching are formed at different temperatures, without any success having been so far attained in identifying by chemical means the character of this branching.

TABLE 8

RELATION BETWEEN THE VISCOSITY AND DEGREE OF POLYMERIZATION OF FRACTIONATED POLYSTYRENES
(Polymerization temperature 32° C) [56]

Osmotic $\overline{P}$	$Z_\eta \times 10^3$	$K_m \times 10^4$ (according to Equation (1))
355	2.03	0.525
655	3.08	0.535
910	4.9	0.50
1010	5.4	0.50
1140	6.3	0.51
1680	9.1	0.505
1880	10.4	0.51
3230	17.4	0.51

On the contrary, with other polyvinyl derivatives, such as polyvinyl chlorides[57], polyvinyl acetates[58], polyacrylic esters[59] and polymethacrylic esters[57], the K_m values always decrease with increase in molecular weight, irrespective of the temperature of polymerization.

The relation between viscosity constant and degree of polymerization can be represented by the equation:

$$Z_\eta = KP^{0.8-0.9} \quad (2)$$

which was derived by Houwink[60] for a series of these products, or by the equation:

$$Z_\eta = KP + b \quad (3)$$

of Schulz and Dinglinger[57].

The reason for the different behavior of these polyvinyl derivatives is still not understood definitely. Possibly they are composed of long but at the same time irregularly twisted macromolecules[60]. In that case, it must be assumed that this irregular form is not so pronounced in hemicolloids as in mesocolloids and eucolloids. Furthermore it is possible that the macromolecules of mesocolloid and eucolloid members are not fibre molecules, but are more or less branched. In this case it would have to be assumed that the branchings increase progressively with increase in the degree of polymerization.

As a contribution to the solution of this problem, the relations between the viscosity constants and the osmotic pressures of mesocolloidal and eucolloidal polyisobutylenes were studied in particular detail. The assumption was made first of all that branchings are probably absent from the macromolecules of this group, just as the macromolecules of hemicolloids are likewise unbranched.

As is shown by the investigations to be described, the viscosity law is applicable to mesocolloidal and eucolloidal polyisobutylenes, but only to the limited extent that it is to the corresponding members of the vinyl derivatives just described, whereas the law is applicable without reservation to hemicolloids, as shown by the experiments described in the previous section.

In Table 9, the $K_{equiv.}$ constants of polyvinyl derivatives known previous to the present work are summarized. The experimental $K_{equiv.}$ constants of low-molecular compounds range from 0.95×10^{-4} to 1.2×10^{-4} in the particular solvents employed. The $K_{equiv.}$ constants of the mesocolloidal and eucolloidal polyisobotylenes are, therefore, only one-half to one-fifth as great as the values found for low-molecular compounds. Here too it is impossible to decide whether the macromolecules of these polyisobutylenes have an irregular twisted structure or whether they are branched. Side reactions are not impossible, since isobutylene is probably never free of traces of other unsaturated hydrocarbons, *e.g.*, butadiene, which may lead to reactions involving branching.

TABLE 9

COMPARISON OF THE $K_{equiv.}$ VALUES OF POLYVINYL COMPOUNDS

Product	Solvent	Average degrees of polymerization	Number of chain members (n)	$K_{equiv.} \times 10^4$
Polyisobutylene	toluene	600–9000	1200–18000	0.25–0.17
Polyvinyl chloride	tetrahydrofuran	1000–2500	2000– 5000	0.52–0.27
Polyvinyl acetate	acetone	850–3650	1700– 7300	0.26–0.12
Polymethyl acrylate	acetone	870–3750	1700– 7500	0.22–0.16
Polymethyl methacrylate	acetone	250–2600	500– 5200	0.27–0.10
Polystyrene	toluene	800–6000	1600–12000	0.2 –0.63

OSMOTIC MEASUREMENTS

As far as their tendency to swell and the viscosity of their solutions are concerned, mesocolloidal and eucolloidal polyisobutylenes behave like linear

colloids, as would be expected from their chemical constitutions. It was, therefore, assumed that their osmotic properties are abnormal, and consequently that the van't Hoff law is not applicable to their solutions, but on the other hand that the p/c values increase with increase in concentration, as is true of solutions of rubber, polymethacrylic esters, nitrocelluloses and polystyrenes[61].

Some osmotic measurements of mesocolloidal and eucolloidal polyisobutylenes in toluene were carried out, and for this purpose the osmometer devised by Schulz[64] was utilized. Surprisingly, the p/c values are approximately constant in this solvent, as is evident from the graphical data in Figure 1.

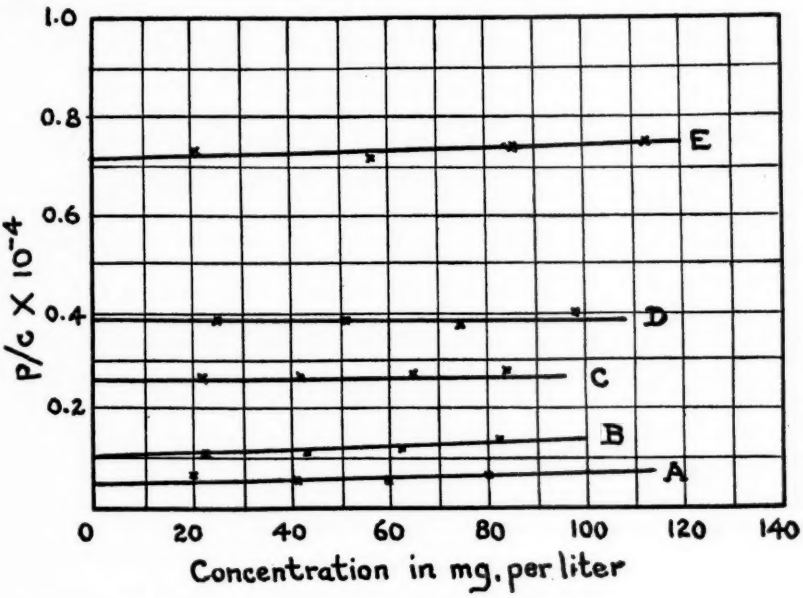


FIG. 1.—Increase in p/c values with increase in concentration (c) of polyisobutylenes in toluene solution at 27° C.

A	Polyisobutylene I	Fraction 1
B	Polyisobutylene I	Fraction 2
C	Polyisobutylene II	Fraction 1
D	Polyisobutylene II	Fraction 2
E	Polyisobutylene II	Fraction 3

With respect to osmotic pressure, solutions of polyisobutylenes in toluene behave like solutions of spherocolloids, which likewise conform to the van't Hoff law. In all other ways, however, they behave like linear colloids. It has been observed in certain other cases that solutions of well-defined linear colloids conform in an approximate way to the van't Hoff law. Thus, for example, the p/c values of polyvinyl chlorides in dioxan[63] and likewise the p/c values of nitrocelluloses in nitrobenzene[64] increase only slightly.

It is evident from numerous investigations that the increase in the p/c values depends to a great extent on the solvent[65]. It may be concluded from these experiments that the deviations from the van't Hoff law are particularly large in solvents in which the dissolved fibre molecules are considerably solvated[66].

It is possible that the approximate constancy of the p/c values of polyisobutylenes in toluene, as well as of nitrocelluloses in nitrobenzene and of polyvinyl chlorides in dioxan, is attributable to the fact that with increase in concentration association takes place, with resulting decrease in the p/c values. If so, then the constancy of the p/c values in these cases is merely fortuitous, and is influenced only by the fact that the increase in the p/c values with increase in concentration is rendered appreciable by the increasing association in concentrated solutions.

To settle this question, osmotic measurements of polyisobutylenes in cyclohexane should be carried out. In this good solvent, these hydrocarbons should

TABLE 10

DETERMINATION OF THE AVERAGE DEGREES OF POLYMERIZATION OF MESOCOLLOIDAL AND EUCOLLOIDAL POLYISOBUTYLENES BY OSMOTIC MEASUREMENTS IN TOLUENE SOLUTIONS AT 27° C

Product	Fraction	Concentration (g. per l.)	$p \times 10^3$	$(p/c) \times 10^3$	$\lim_{c \to 0} p/c$	$\bar{M}$	$\bar{P}$
Polyisobutylene I	1	2.00	0.15	0.08			
		4.10	0.26	0.06			
		5.90	0.38	0.06	0.05	500,000	9000
		8.00	0.57	0.07			
		10.00	0.83	0.08			
	2	2.20	0.23	0.10			
		4.18	0.44	0.11	0.10	240,000	4500
		6.20	0.77	0.12			
		8.20	1.12	0.14			
Polyisobutylene II	1	2.13	0.58	0.27			
		4.14	1.11	0.27			
		6.54	1.77	0.27	0.27	91,000	1600
		8.40	2.38	0.28			
	2	2.54	0.98	0.39			
		5.04	1.97	0.39	0.39	63,000	1100
		7.57	2.88	0.38			
		9.87	4.05	0.41			
	3	2.62	1.90	0.73			
		5.69	4.09	0.72	0.72	34,000	600
		8.39	6.22	0.74			
		11.30	8.49	0.75			

behave like other linear molecular substances, and the p/c values should increase with increasing concentration. On the contrary, in benzene, a particularly poor solvent, the p/c value should decrease with increase in concentration still more than in toluene, assuming that association takes place at higher concentrations. According to experiments of Dobry on nitrocelluloses, the lim p/c values of nitrocelluloses in different solvents are essentially the same, for in very dilute solutions, macromolecules are present in all cases in the dissolved state. It may, therefore, be assumed that the average molecular weights of polyisobutylenes can be calculated from their lim p/c values in toluene (see Table 10). Whether or not this assumption is justified can be decided only when the lim p/c values in different solvents are determined under the same conditions.

The question whether macromolecules or associations of molecules are present in dilute solutions in toluene can be answered by determining the

osmotic pressure at various temperatures. If the lim p/c values increase with increase in temperature in accordance with the law of van't Hoff, then macromolecules are present. If, on the contrary, the macromolecules are associated, these associations would at elevated temperatures break up into individual molecules, and this dissociation would be manifest by a marked increase in the p/c values[67].

DETERMINATION OF THE $K_{equiv.}$ CONSTANTS OF MESOCOLLOIDAL AND EUCOLLOIDAL POLYISOBUTYLENES IN TOLUENE

The viscosity constants of the five polyisobutylenes whose average degrees of polymerization were determined by osmotic measurements in toluene solutions were determined in the same solvent. In addition, the relation between viscosity and temperature was ascertained by determining the ratios of the Z_η values at 60° C to the Z_η values at 20° C. This ratio of Z_η at 60° C to Z_η at 20° C was found to be greater than 1, as is evident from the data in Table 11, whereas it is approximately 0.8–0.9 for products of low molecular weight[68]. That the viscosity constants at 60° C are higher than those at 20° C can perhaps be attributed to the fact that at relatively low temperatures mesocolloidal and eucolloidal polyisobutylenes are not in solution in macromolecular form, but that associations of molecules are still present, and that these dissociate at higher temperatures.

From the average degrees of polymerization, $\overline{P}$, shown in Table 10, the average numbers of chain members, $\overline{n}$, of these polyisobutylenes were calculated, and from their viscosity constants recorded in Table 11 their $K_{equiv.}$ constants were likewise calculated.

TABLE 12

$K_{equiv.}$ VALUES OF MESOCOLLOIDAL AND EUCOLLOIDAL POLYISOBUTYLENES IN TOLUENE

Polyisobutylene	Fraction	$\overline{P}$	n	Z	$K_{equiv.} \times 10^{-4}$
I	1	9000	18,000	0.410	0.23
	2	4500	9,000	0.170	0.19
II	1	1600	3,200	0.054	0.17
	2	1100	2,200	0.044	0.20
	3	600	1,200	0.031	0.25

The K_{equiv} constant of low-molecular substances in toluene is 0.95×10^{-4}. If the molecular weights of these polyisobutylenes are calculated from their viscosity constants by means of these constants, the values calculated in this way are only about one-fifth of the true values obtained experimentally by osmotic measurements. The average number of chain members D_n calculated with the constant 0.95×10^{-4} represents only the length of the long straight molecules in solution, if it is assumed, in calculating the length of such a long straight molecule in solution, that the viscosity law is valid. The justification for this assumption rests on the fact that the viscosity law is applicable to mesocolloidal and eucolloidal celluloses.

VISCOSITY MEASUREMENTS OF MESOCOLLOIDAL AND EUCOLLOIDAL POLYISOBUTYLENES

To study the temperature effect in various solvents, the viscosity constants at 20° and at 60° C of 0.2 per cent solutions of a series of mesocolloidal and

eucolloidal polyisobutylenes were determined. The average degrees of polymerization of these products were estimated from viscosity measurements with the help of their viscosity constants and the $K_{equiv.}$ constant 0.2×10^{-4}. The data in Table 13 show that the temperature coefficient of cyclohexane solutions and of carbon tetrachloride solutions is less than 1; in other words, the viscosity constants in these cases are less at 60° C than at 20° C, as is true of compounds of low molecular weights. The small increase in the case of the products with the highest molecular weights may be attributable to the presence in this case too of associations of molecules in solution.

On the other hand, the great temperature effect on the viscosity constants in benzene is surprising; in fact this effect is so great that at 60° C the viscosity constants of a eucolloidal polyisobutylene are more than twice as great as the viscosity constants at 20° C. This may be explained on the assumption that eucolloidal polyisobutylenes do not form solutions of the normal kind in benzene. However, this question will be answered by further investigation.

TABLE 13

TEMPERATURE EFFECT ON THE VISCOSITY CONSTANTS OF 0.2 PER CENT SOLUTIONS OF MESOCOLLOIDAL POLYISOBUTYLENES AND OF EUCOLLOIDAL POLYISOBUTYLENES IN VARIOUS SOLVENTS

Average degree of polymerization	Ratio of $Z\eta$ at 60° C to $Z\eta$ at 20° C		
	in cyclohexane	in carbon tetrachloride	in benzene
260	0.83	0.84	0.90
590	0.87	0.90	1.09
1200	0.94	0.97	1.51
1700	0.95	0.96	1.94
2600	0.95	0.98	2.15

REFERENCES

[1] Hemicolloidal polyisobutylenes were investigated in 1936 by one of the present authors (G. Berger), and eucolloidal polyisobutylenes in 1939 and 1940 by another of the present authors (Kl. Fischer). These investigations had to be suspended because of the induction into the service of the latter investigator. Because of the technical importance of polyisobutylene, the investigations are published at the present time in spite of their incompleteness.

[2] Staudinger, "Die hochmolekularen organischen Verbindungen: Kautschuk und Cellulose," Julius Springer, Berlin, **1932**, p. 39.

[3] See, for example, the older theories of micelles of Karrer, Hess, Bergmann and Pummerer, and the more recent theories of Meyer (*Z. angew. Chem.* **41**, 935 (1928).

[4] For the classification of organic colloids, see Staudinger, "Organische kolloidchemie", 2nd Ed., Verlag Vieweg, Braunschweig, **1941**, p. 124.

[5] Staudinger and collaborators, *Helv. Chim. Acta* **12**, 934 (1929).

[6] Staudinger and Dreher, *Ann.* **517**, 73 (1935).

[7] Staudinger and collaborators, *Ber.* **62**, 241 (1929). Polystyrene was the first example chosen for studying the changes in properties of polymeric substances with increasing degree of polymerization.

[8] Waterman and Leendertse, *Rec. trav. chim.* **54**, 139 (1935): *Trans. Faraday Soc.* **53**, 231 (1936).

[9] Schwarz, *Kautschuk* **13**, 183 (1937); Sparks, Lightbown, Turner, Frolich and Klebsattel, *Ind. Eng. Chem.* **32**, 731 (1940); *Kunststoffe* **30**, 380 (1940); Springer, *Kunststoffe* **30**, 291 (1940).

[10] Lebedev and Filonenko, *Ber.* **58**, 163 (1925).

[11] Waterman, Over and Tulleners, *Rec. trav. chim.* **53**, 699 (1934); Leendertse, Tulleners and Waterman, *Rec. trav. chim.* **52**, 515 (1933).

[12] Staudinger and Brunner, *Helv. Chim. Acta* **13**, 1375 (1930).

[13] Hofmann, *Chem.-Ztg.* **57**, 5 (1933); Hofmann and Otto, French patent 532,768 (*Chem. Zentr.* **1928**, II, 1035); German patent 513,862 (*Chem. Zentr.* **1932**, I, 1713); 505,265 and 512,959 (*Chem. Zentr.* **1931**, II, 4094).

[14] Thomas, Sparks, Frolich, Otto and Mueller-Cunradi, *J. Am. Chem. Soc.* **62**, 276 (1940).

[15] Staudinger and collaborators, *Ber.* **62**, 241 (1929); Schulz and Husemann, *Z. physik. Chem.* [B] **34**, 187 (1936).

[16] Polycondensation processes proceed otherwise, for in such cases, the products formed at relatively high temperatures have higher molecular weights than those formed at lower temperatures. See, for example, the formation of superpolyesters according to Carothers.

[17] A series of polymers was kindly placed at our disposal by the management of the I. G. Farbenindustrie A.-G., Ludwigshafen, for which we express our appreciation at this time.

[18] The microanalyses were made by S. Kautz.

[19] Whitmore, *Ind. Eng. Chem.* **26**, 94 (1934).

[20] Staudinger and Frost, *Ber.* **68**, 2351 (1935). See in particular the extensive investigations of these chain reactions by Schulz (*Ergebnisse der exakten Naturwissenschaften* **18**, 367 (1938); "Fortschritte der Chemie, Physik und Technik der macromolekularen Stoffe", München, **1939**, p. 29).

[21] Thomas, Sparks, Frolich, Otto and Mueller-Cunradi, *J. Am. Chem. Soc.* **62**, 279 (1940).

[22] Staudinger and Steinhofer, *Ann.* **517**, 35 (1935).
[23] Staudinger and Schwalbach, *Ann.* **488**, 8 (1931).
[24] With respect to the position of the substituents in polymeric products, see Marvel and Denoon, *J. Am. Chem. Soc.* **60**, 1045 (1938); Levesque, *J. Am. Chem. Soc.* **60**, 280 (1938); **61**, 1682, 3234 (1939); Levesque and Cowan, *J. Am. Chem. Soc.* **61**, 3156 (1939).
[25] For the influence of impurities on polymerization, see Thomas, Sparks, Frolich, Otto and Mueller-Cunradi, *J. Am. Chem. Soc.* **62**, 279 (1940).
[26] Styrene, which contains small percentages of divinylbenzene, yields an insoluble polystyrene with limited tendency to swell in solvents (cf. Staudinger and Heuer, *Ber.* **67**, 1164 (1618 (1935); Staudinger and Husemann, *Ber.* **68**, 1618 (1935)). Very small percentages of divinylbenzene lead to soluble products with strongly branched molecules.
[27] Staudinger, *Helv. Chim. Acta* **13**, 1332 (1930).
[28] Kirchhof, *Kolloid-Z.* **30**, 176 (1922); *Kautschuk* **6**, 31, (1930); Fikentscher and Mark, *Kautschuk* **6**, 5 (1930).
[29] Staudinger, *Helv. Chim. Acta* **13**, 1332 (1930); *Ber.* **63**, 921 (1930).
[30] To what extent saturated and unsaturated hydrocarbons of the same chain length differ in elasticity has not yet been determined with any degree of precision.
[31] Staudinger and Machemer, *Ber.* **62**, 2922 (1929).
[32] Kuhn, *Kolloid-Z.* **68**, 2 (1934); **76**, 258 (1936); *Z. angew. Chem.* **49**, 858 (1936); **51**, 642 (1938).
[33] Brill and Halle, *Naturwissenschaften* **26**, 12 (1938); Fuller, Frosch and Pape, *J. Am. Chem. Soc.* **62**, 1905 (1940).
[34] Staudinger, "Organische Kolloidchemie", 2nd Ed., Verlag Vieweg, Braunschweig, **1941**, p. 206.
[35] Wöhlisch, in his first work on kinetics, accepted the static theory of elasticity of rubber, *i.e.*, that rubber particles are elongated and at the same time rigid (cf. *Vereinigte physikalisch-medizinische Gesellschaft*, Wurzburg, N. F. **51**, 253 (1926); *Kolloid-Z.* **89**, 239 (1939).
[36] Staudinger and Fischer, *J. prakt. Chem.* [2] **57**, 19 (1940); **157**, 158 (1940); **158**, 304 (1941).
[37] Side chains in long straight fibre molecules increase elasticity; they function in an analogous way to the addition of softening agents in increasing elasticity (cf. Staudinger and Machemer, *Ber.* **62**, 2922 (1929); Ueberreiter, *Z. physik. Chem.* **46B**, 157 (1940).
[38] Schulz, *Z. physik. Chem.* **179A**, 321 (1937); Schulz and Jirgensons, *Z. physik. Chem.* **46B**, 155 (1940).
[39] Staudinger and Heuer, *Z. physik. Chem.* **171A**, 129 (1934).
[40] See the molecular-weight determinations by precipitation titration of Schulz (*Z. physik. Chem.* **179A**, 321 (1937); Schulz and Jirgensons, *Z. physik. Chem.* **46B**, 105 (1940). These determinations are to be extended to polyisobutylenes as well.
[41] For an abnormal paraffin of high molecular weight, see Fischer and Tropsch (*Ber.* **60**, 1330 (1927)), Pichler (*Z. angew. Chem.* **51**, 412 (1938)), and Fischer and Pichler (*Ber.* **72**, 327 (1939)).
[42] Staudinger and Leupold, *Helv. Chim. Acta* **15**, 221 (1932).
[43] Staudinger and Leupold, *Ber.* **67**, 304 (1934).
[44] Mayer and Mark, *Ber.* **61**, 1939 (1928).
[45] Whereas in the past it has been generally assumed that colloidal particles in solutions of high molecular substances have a micellar structure, many investigators today believe implicitly that such colloidal particles have a macromolecular structure. It should be pointed out that the macromolecular structure of colloidal particles can be proved beyond doubt only by polymerically analogous transformations.
[46] In solutions of ethylcellulose with free OH groups in benzene, the colloidal particles are not the macromolecules themselves, but are associations of these macromolecules, and therefore are supermolecules (cf. Staudinger and Reinecke, *Ann.* **535**, 71 (1938); Steurer, *Kolloid-Z.* **96**, 333 (1941).
[47] Staudinger and collaborators, *Ber.* **62**, 251 (1929); *Kolloid-Z.* **54**, 137 (1931).
[48] Staudinger and Machemer, *Ber.* **62**, 2921 (1929); Staudinger, "Organische Kolloidchemie", Verlag Vieweg, **1941**, p. 107.
[49] Staudinger and Staiger, *Ber.* **68**, 707 (1935).
[50] Staudinger and Mojen, *Kautschuk* **12**, 121 (1936).
[51] Hess and collaborators, "Chemie der Cellulose", Leipzig, **1928**, Staudinger and Schulz, *Ber.* **70**, 1577 (1937).
[52] Staudinger and Dreher, *Ann.* **517**, 73 (1935); Staudinger, Kern and Herrera, *Ber.* **68**, 2346 (1935).
[53] Staudinger, "Organische Kolloidchemie", Verlag Vieweg, Braunschweig, **1941**, p. 73.
[54] Staudinger, "Organische Kolloidchemie", 2nd Ed., Verlag Vieweg, Braunschweig, **1941**, p. 92.
[55] Staudinger and Schulz, *Ber.* **68**, 2320 (1935); Schulz and Husemann, *Z. physik. Chem.* **36B**, 184 (1937); Schulz, *Z. physik. Chem.* **44B**, 227 (1939).
[56] Schulz and Dinglinger, *J. prakt. Chem.* [2] **158**, 136 (1941).
[57] Staudinger and Schneiders, *Ann.* **541**, 151 (1939).
[58] Staudinger and Warth, *J. prakt. Chem.* [2] **155**, 261 (1940).
[59] Houwink, *J. prakt. Chem.* [2] **157**, 15 (1940).
[60] Staudinger, "Organische Kolloidchemie", 2nd Ed. Verlag. Vieweg, Braunschweig, **1941**, p. 217.
[61] Staudinger and Schulz, *Ber.* **68**, 2320, 2336 (1935).
[62] Schulz, *Z. physik. Chem.* **176A**, 317 (1936); "Fortschritte der Chemie, Physik und Technik der makromolekularen Stoffe", Vol. II, Verlag Lehmann, **1942**, p. 49.
[63] Staudinger and Schneiders, *Ann.* **541**, 151 (1939).
[64] Dobry, *J. chim. phys.* **12**, 50 (1935); *Bull. soc. chim.* **22**, 1882 (1935).
[65] Dobry, *Kolloid-Z.* **81**, 190 (1937); Schulz, "Fortschritte der Chemie, Physik und Technik der makromolekularen Stoffe", Vol. II, Verlag Lehmann, **1942**, p. 49.
[66] Schulz, *Z. physik. Chem.* **176A**, 317 (1936); **184**, 1 (1939).
[67] For osmotic measurements of nitrocelluloses and polystyrenes at various temperatures, see Schulz, *Z. physik. Chem.* **180A**, 1 (1937); **40B**, 319 (1938).
[68] Staudinger, "Die hochmolekularen organischen Verbindungen: Kautschuk und Cellulose", Verlag Julius Springer, **1932**, pp. 85 and 171; Staudinger and Staiger, *Ber.* **68**, 715 (1935).

STRUCTURE OF COPOLYMERS OF ISOBUTYLENE AND ISOPRENE *

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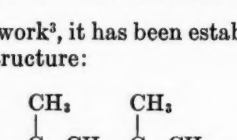
Rubberlike materials prepared by low-temperature copolymerization of isobutylene with isoprene[1] constitute part of a more general class of olefin-diolefin copolymers now known arbitrarily as Butyl rubber. Since the physical and chemical properties of the copolymers would be expected to depend on the manner in which the diolefin units enter the polymer chain, a study was made of several of these copolymers containing various percentages of isoprene units.

The use of ozone degradation for determining the structure of organic compounds containing olefinic double bonds has been extended in recent years to natural and synthetic rubbers with a considerable degree of success[2] and has served to reveal the structure of these polymers to an extent not attainable either by other chemical methods or by indirect physical and optical methods. The general procedure consists of adding a molecule of ozone to each double bond, cleaving the resulting ozonide by hydrolysis or reduction, identifying the fragment molecules, and reconstructing the original molecule on the basis of this analysis. This method was applied in a study of the isobutylene-isoprene copolymers. In the latter case experimental difficulties arise mainly because of the low degree of unsaturation that these polymers possess; the amount of fragment molecules obtained is quite small, and the properties of the solvent medium therefore assume a relatively more important role than is the case with other rubberlike materials, which contain comparatively many double bonds.

OCCURRENCE OF SINGLE ISOPRENE UNITS

As the result of previous work[3], it has been established that polyisobutylenes possess the "head-to-tail" structure:



The similarity between the x-ray fiber diagrams for several isobutylene-isoprene copolymers[4] and that of polyisobutylene[5] makes plausible the assumption that the structure above also exists in that part of the copolymer chain adjacent to the isoprene units. In regard to the manner in which the latter units enter the polymer chain, an error in this assumption is immaterial because of the saturated character of the polyisobutylene sections of the molecule.

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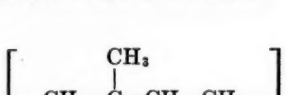
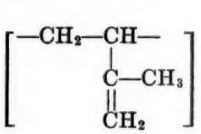
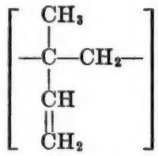
Three possible structures, or mixtures of these, can be written to represent the mode of isoprene addition:



Structure I



Structure II



Structure III

A random entry of the diolefin into the growing chain would result in structures $-A_nBA_nBA_n-$ in which diolefin residues B are separated from one another by many isobutylene units A; the value of n (which is of the order of 50–200, as indicated by measurements of unsaturation) depends on the particular polymer. Preferred addition, on the other hand, would result in regions where n is smaller, so that one would then have groups of two or more B units separated by proportionately fewer A units.

Ozonolysis of a linear molecule having structure I would give only aldehydes or acids having $(2n + 4)$ chain carbon atoms, except for formaldehyde or formic acid contributed by terminal double bonds. The latter contribution would be extremely minute for polymers of the high molecular weights here investigated, and would not be capable of detailed analysis by the present methods. Alternatively, ozonolysis of structures II or III would yield one molecule of either formaldehyde or formic acid for each side-chain methylene group, but the detection of these degradation products would not serve to distinguish between II and III.

EXPERIMENTAL PROCEDURE

The polymers selected for this work consisted of a series containing 0.6, 0.9, and 2.4 moles of isoprene units per 100 isobutylene units, as determined by unsaturation methods to be described elsewhere[6]. In addition, a polyisobutylene that had been fractionated[7] in such a way as to remove all species having viscosity-average molecular weights less than 50,000 was included because of its interest as a limiting case, this polymer having only 0.02 mole per cent of unsaturation. After some preliminary experiments, the following method was chosen for ozonization. About 5 grams of polymer dissolved in 100–150 cc. of solvent were cooled to 0° C in an all-glass apparatus with the reaction flask immersed in cracked ice and equipped with a four-tube reflux condenser. Ozonized air containing about 2.5 volume per cent of ozone was passed through concentrated sulfuric acid and Drierite, and then into the reaction flask at a rate of approximately 15 cc. per second for 4 hours. It is apparent from Figure 1 that, under these conditions, the degradation process is terminated in about half of this time. These curves were obtained by recovering the polymer at various intervals and determining its intrinsic viscosity in diisobutylene at 20° C. The total amount of ozone delivered during the run was about 20 per cent by weight, based on the polymer.

To cleave any ozonides that might have remained intact, the ozonized solution was then refluxed with previously boiled, distilled water for one hour in an all-glass apparatus, the condenser of which was equipped with a soda-lime trap to exclude atmospheric carbon dioxide. The aqueous extract was allowed to cool to room temperature and was immediately titrated with 0.01 N potassium hydroxide to a phenolphthalein end-point, and the neutralized solution

divided into two portions. One portion was analyzed for the presence of formate by reacting the latter with mercuric chloride to give mercurous chloride, which was determined gravimetrically. The other portion was analyzed for aldehydes by means of dimethyldihydroresorcinol[8]. A parallel set of experiments in which the ozonized solution was hydrolyzed at room temperature by strong mechanical agitation with previously boiled, distilled water served to

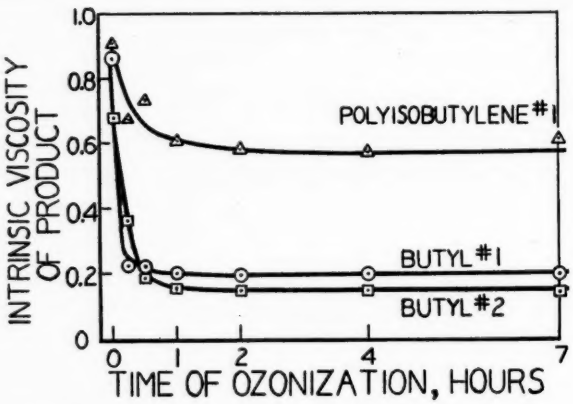


FIG. 1.—Rate of degradation of polyisobutylene and butyl rubber by ozone (0.25 volume per cent ozonized air).

show that the absence of aldehydes was not due to volatilization during refluxing, and also established that the increase in acidity of the aqueous extract during the refluxing step was not due to formic acid and was therefore attributable to other sources discussed below.

PROPERTIES OF SOLVENT

Chloroform that had been further purified[9] and stored in the dark was used as solvent in the first experiments. However, the ozonization of this substance yielded undesirably large and variable acidity values, and the aqueous extract gave a positive chloride test, an indication that the reaction[10]:

$$CHCl_3 + O_3 \rightarrow COCl_2 + HCl + O_2$$

may occur to a disturbing extent even at 0° C and with dilute ozonized air. The solvent was then changed to carbon tetrachloride; when this substance

TABLE I

ACIDITY OF AQUEOUS EXTRACTS OF PURIFIED CARBON TETRACHLORIDE

Freshly distilled solvent	Before refluxing		After refluxing	
	Total acidity[a]	Formic acid[b]	Total acidity[a]	Formic acid[b]
Batch A	0.34	..	0.90	..
Batch B	0.36	..	1.88 (?)	..
Batch C	0.30	19.6	0.80	16.4
Batch D+catalyst[c]	0.44	9.6	0.50	4.0

[a] Expressed as ml. of 0.01 *N* KOH per 100 cc. CCl_4.
[b] Expressed as mg. of HgCl per 100 cc. CCl_4.
[c] 150 cc. fresh solvent allowed to stand in dark for 2 days in presence of 0.01 gram of the catalyst utilized in synthesizing the polymers investigated in this work, filtered, and tested.

was suitably purified[9], it could be employed without encountering complications due to appreciable solvent decomposition. Acidic properties of this solvent under different conditions are given in Table I. The acidity values include a titration error of 0.2 cc. obtained with a previously boiled, distilled water, control titration.

Since the polymer solutions were to be treated with ozonized air, it was necessary to determine the effect of the latter on the solvent. Table II shows the effects of air and of 0.25 per cent ozonized air on the solvent under the conditions employed in the ozonization procedure.

TABLE II

EFFECT OF AERATION ON ACIDITY OF AQUEOUS EXTRACTS OF CARBON TETRACHLORIDE AT 0° C

Batch	Nature of solvent	Before refluxing		After refluxing	
		Total acidity[a]	Formic acid[b]	Total acidity[a]	Formic acid[b]
	a. Effect of air				
A	Freshly distilled	0.42	..	0.86	..
A	4 days old	0.38	..	0.72	..
A	4 days old, aerated, stored 2 days	0.38	..	1.12	..
B	Freshly distd.	0.50	14.0	0.90	5.6
C	Several days old + catalyst[c]	0.38	4.4	0.58	12.8
	b. Effect of ozonized air				
A	Freshly distilled	0.48	..	1.26	*c*
A	4 days old	1.06	..	3.12	..
B	Freshly distilled	0.63	4.8	4.05	8.0
C	Several days old + catalyst[c]	0.96	12.4	2.56	9.6
D	Several days old + catalyst[d]	1.50	8.0	3.60	22.5

[a] Expressed as cc. of 0.01 *N* KOH per 100 ml. CCl_4.
[b] Expressed as cc. of HgCl per 100 cc. CCl_4.
[c] 150 cc. of old solvent allowed to stand in dark for 2 days in presence of 0.01 gram of polymerization catalyst, filtered, ozonized, and tested.
[d] Same as [c], except that ozonization was carried out in presence of catalyst.

The data in Tables I and II enable the following observations to be made:

1. The acidity of the solvent is independent of its age over a period of at least several days, and is not affected significantly by allowing the solvent to stand for 2 days in the presence of an amount of the polymerization catalyst in excess of that introduced as a polymer impurity during preparation of the solutions.

2. When the solvent is refluxed with water at the boiling point of the former, the acidity is increased by a factor of 2–3.

3. The passage of air through the solvent has little effect on its acidity. Previous contact with the catalyst is not a disturbing factor. When the aerated solvent is refluxed with water, the increase in acidity is no greater than that observed in the absence of aeration.

4. The passage of ozonized air through the solvent at 0° C has little effect on its acidity unless the solvent is several days old. In the latter case, the acidity is roughly doubled. Previous contact of the solvent with the catalyst has little additional effect. When the ozonized solvent is refluxed with water, the increase in acidity exceeds that obtained with aerated solvent by a factor of 2–3. This is attributed to the action of dissolved ozone at the elevated temperature.

RELIABILITY OF ANALYTICAL METHOD

If, in Tables I and II, a comparison is made of the total acidity and the formic acid data, an important discrepancy is noted. It was mentioned above that the aqueous extracts were analyzed for formic acid by means of the well-known reaction[11]:

$$2HgCl_2 + HCOONa \rightarrow 2HgCl + NaCl + HCl + CO_2$$

In accordance with this reaction, 1 cc. of 0.01 *N* formic acid is equivalent to 4.7 mg. of mercurous chloride. On the basis of this ratio, the mercurous chloride data listed in the tables are equivalent in most cases to amounts of formic acid that exceed considerably the corresponding values of total acidity. Since this is absurd, the question arises as to whether the mercurous chloride method is quantitative for the solutions investigated. To answer this question, an independent analytical method for determining formic acid was applied. The latter is based on the fact that, when formic acid or formate solutions are treated with magnesium, the formate ion is reduced to formaldehyde[12]. Aliquot parts of all the solutions for which the mercurous chloride data were obtained were treated according to this method and then tested for the presence of formaldehyde by dimethyldihydroresorcinol[8]. The latter test was applied also to all of the solutions for which no mercurous chloride data were obtained. By means of control tests carried out with known solutions of formaldehyde, confirmation was found for Weinberger's claim[8] that the above reagent will detect as little as 0.2 mg. of formaldehyde in 50 cc. of solution. Despite the sensitivity of this test, no indication was found of the presence of formaldehyde in any of the aqueous extracts examined. This result is considered to be strong evidence for the view that the mercurous chloride analysis cannot be safely applied in determining the possible presence of formic acid in such solutions as were studied in this work. Therefore, in the subsequent work with the polymer solutions, only the reduction method of Fenton and Sisson[12], combined with the Weinberger method, was used for formic acid.

The interference caused by the possible presence of very small amounts of aldehydes[13], lower-molecular-weight fatty acids[14], or chlorides[15] cannot be held responsible for the erroneous mercurous chloride results, since these interfering substances lead to low, rather than high, values.

OZONOLYSIS OF 1-PENTENE AND 2-METHYL-1-PENTENE

Since the terminal methylene group in 1-pentene is similar to that which would exist in the isoprene residue in a 3,4 addition polymer (structure III), while that in 2-methyl-1-pentene would correspond to that in 1,2 addition (structure II), a control experiment was run to ozonize these hydrocarbons under the conditions employed with the Butyl polymers. Solutions containing 0.1 cc. of hydrocarbon in 150 cc. of purified carbon tetrachloride were used, this concentration corresponding roughly to the concentration of double bonds existing in the polymer solutions. The following acidity data were obtained, expressed as cc. of 0.01 *N* potassium hydroxide per 100 cc. of solution:

Solution	Extract	1-Pentene	2-Methyl-1-pentene
Original	Aqueous	0.40	0.60
Ozonized	Aqueous	17.3	4.8
Ozonized	Aqueous, after refluxing	33.6	11.8

The original solution of 1-pentene was tested for formaldehyde and formic acid, and none could be detected. The ozonized solutions, however, gave aqueous extracts with very positive formaldehyde tests. A trace of formaldehyde was detected in the original solution of 2-methyl-1-pentene, but considerably more was found after ozonization, both before and after refluxing.

These results indicate that the experimental conditions employed are adequate to reveal the existence of 1,2 or 3,4 addition in the polymers, unless the diolefin units constitute only an extremely small percentage of the double bonds present.

OZONOLYSIS OF POLYISOBUTYLENE

An ozonolysis experiment carried out with 4.7 grams of the polyisobutylene fraction (0.02 mole per cent unsaturation) dissolved in 100 cc. of solvent served as an additional control, since no isoprene had been used in the synthesis of this polymer. The following acidity values, in cc. of 0.01 *N* potassium hydroxide per 100 cc. of solution, were obtained:

Original solution, aqueous extract, 0.70
Ozonized solution, aqueous extract, 4.1
Ozonized solution, aqueous extract after refluxing, 7.6

The three aqueous extracts were analyzed for formaldehyde and formic acid; none could be detected. Comparison of the acidity values with those in Table II*b* shows that the former are about twice as large as those obtained by ozonizing the solvent alone. This difference is readily attributable to the hydrolysis of small amounts of residual catalyst in the polymer, to end groups, and to acids formed by oxidative degradation.

Effect of residual catalyst.—The polyisobutylene used in the above experiment had been prepared with boron trifluoride as catalyst, and was found to contain approximately 0.01 per cent of this material (determined as boron). Assuming the latter to be present in the polymer as BF_3, it is easily shown that complete hydrolysis of the residual catalyst in a 5-gram sample of the polymer will give rise to sufficient hydrofluoric acid to require 2.2 cc. of 0.01 *N* potassium hydroxide for neutralization, neglecting the boric acid formed in the hydrolysis.

Effect of end groups.—The polyisobutylene fraction was found to have a viscosity average molecular weight of 700,000[7]. After ozonization this value decreased to 590,000. Assuming that both chain termini in the degraded polymer existed as carboxyl groups, the latter would require about 3.2 cc. of 0.01 *N* potassium hydroxide for a 5-gram sample.

The two factors just considered therefore seem most likely to have been responsible for the increased acidity observed when the polymer solution was ozonized. The absence of formaldehyde or formic acid in the aqueous extracts confirmed the expectation that no appreciable number of side-chain methylene groups were present in the polymer chain and further established the validity of the ozonization method.

OZONOLYSIS OF ISOBUTYLENE-ISOPRENE COPOLYMERS

Butyl sample 1.—This polymer sample was found to have a viscosity average molecular weight of 500,000, an unsaturation value of 0.6 mole per cent of isoprene, and about 0.11 per cent of residual catalyst. A 4.7-gram sample was dissolved in 100 cc. of carbon tetrachloride and ozonized as previously described.

The following acidity values were obtained:

Original solution, aqueous extract, 1.1
Ozonized solution, aqueous extract, 4.1
Ozonized solution, aqueous extract after refluxing, 14.7

No formaldehyde or formic acid could be detected in the aqueous extracts. By a computation analogous to that mentioned above for polyisobutylene, it was found that complete hydrolysis of the residual catalyst in this sample would lead to an acidity value of 12; this, together with the solvent and end-group contributions, would give a figure in good agreement with 14.7 obtained for the aqueous extract after refluxing.

The absence of formaldehyde or formic acid in the aqueous extracts indicates the absence of side-chain methylene groups in the polymer molecule. A copolymer sample weighing 4.7 grams and containing 0.6 mole per cent isoprene unit, present entirely as 1,2 or 3,4 addition products, would give an equivalent of 150 mg. of formaldehyde, half of which would be present in the portion taken for refluxing. Since the analytical method used in these experiments was capable of detecting 0.2 mg. of formaldehyde in the 50 cc. of aqueous extract employed, not more than about 3 isoprene units in 1000 could have other than the 1,4 position.

Since it is conceivable that a greater proportion of the isoprene units might have been present in the 1,2 or 3,4 positions but escaped detection because of complete oxidation of their methylene groups to carbon dioxide, experiments were carried out in which the ozonized air stream was passed from the polymer solution through saturated barium hydroxide; the carbon dioxide content was determined as barium carbonate. Under comparable conditions the polymer solution gave rise to 0.126 gram of the carbonate, while the solvent control gave 0.128 gram. Therefore no carbon dioxide was formed that could be attributed to the polymer. Similar experiments were carried out with Butyl sample 2. In that case 0.057 gram of the carbonate was formed, while the pure solvent gave 0.056 gram. It is therefore apparent that the conditions of ozonization employed are not sufficiently drastic to oxidize the polymer groups to the carbon dioxide stage.

Experiments with Butyl samples 1 and 2 were also carried out in which the effluent gas stream was passed through dilute sodium hydroxide, and the latter analyzed for formic acid and formaldehyde. Neither was found, and it was therefore established that the inability to detect these degradation products in the extracts of the ozonized polymer solutions could not be attributed to loss in the gas stream.

Butyl sample 2.—This polymer sample contained 0.9 mole per cent unsaturation, about 0.20 per cent of residual catalyst, and had a viscosity average molecular weight of 450,000. Ozonolysis of a 4.7-gram sample gave the following acidity values:

Original solution, aqueous extract, 12.7
Ozonized solution, aqueous extract, 9.6
Ozonized solution, aqueous extract after refluxing, 47.3

No formaldehyde or formic acid was found in the aqueous extracts. About 20 cc. of the total acidity could be attributed to residual catalyst, while the remainder is believed to have arisen mainly from oxidation products in the original polymer. The negative tests for formaldehyde and formic acid indicate that not more than 2 isoprene units in 1000 could have been present in the 1,2 or 3,4 positions.

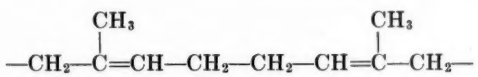
Butyl sample 3.—This sample had a viscosity average molecular weight of 500,000 and an unsaturation value of 2.4 mole per cent. The size of the sample was inadequate for obtaining an analysis of residual catalyst. The material had stood in the laboratory for some time, and as judged by its appearance, some superficial oxidation had occurred. Ozonolysis of a 2.7-gram sample gave the following acidity values, which have been corrected to the same basis of comparison as the preceding polymers:

Original solution, aqueous extract, 2.0
Ozonized solution, aqueous extract, 14.0
Ozonized solution, aqueous extract after refluxing, 48.2

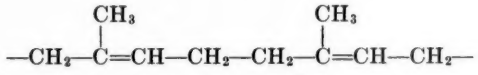
Neither formaldehyde nor formic acid could be detected in the extracts; the absence of the latter indicated that less than 1 isoprene unit in 1000 had the 1,2 or 3,4 position.

SEQUENCE OF ISOPRENE UNITS IN POLYMER MOLECULE

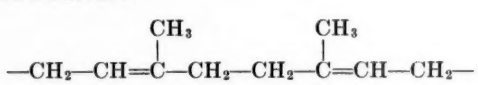
If, during the formation of the polymer chain, the entry of diolefin molecules into the polymer does not take place at random, then several possible structures are possible in which two (or more) of the isoprene units may occupy adjacent positions in the molecule. Ozonization of a molecule containing the tail-to-tail structure:



should yield succinaldehyde or succinic acid. Ozonization of the heat-to-tail structure:



should give rise to levulinic aldehyde or levulinic acid. The third possibility is the head-to-head structure:



which should yield acetonylacetone.

Since the possible degradation products are readily soluble in water, the technique adopted consisted in ozonizing the polymers in the manner previously described, and analyzing the aqueous extracts for the presence of the above products. Ten grams of polymer that had been dried in a vacuum at 60–70° C were dissolved in 150 cc. of purified carbon tetrachloride and ozonized at 0° for 3 hours. The degraded solution was extracted with two 25-cc. portions of previously boiled, distilled water by strong mechanical agitation for 1-hour periods. To the combined extracts were added 10 cc. of 7 per cent hydrogen peroxide (to oxidize aldehydes that might have been present); the mixture was agitated for 3 hours and then heated with a slight excess of sodium hydoxide until evolution of unreacted hydrogen peroxide had ceased. The solution was then carefully neutralized with dilute nitric acid and divided into three equal parts:

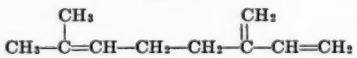
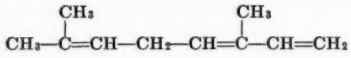
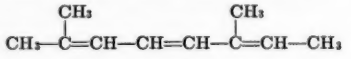
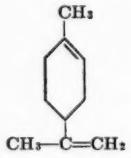
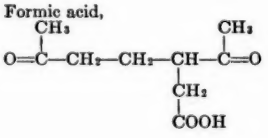
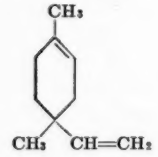
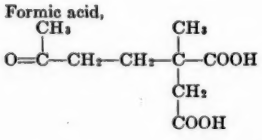
1. One part was tested for succinic acid by adding an equal volume of 9 per cent lead acetate solution; the mixture was then diluted with an equal volume of ethanol. The precipitated lead salt was analyzed to establish

whether it was the succinate. Repeated experiments with samples of Butyl 1 gave 0.03–0.21 gram of lead salt; experiments with Butyl 2 gave 0.13–0.22 gram. That these precipitates did not consist of lead succinate is shown by the following typical analysis: lead, 76.97, 76.88; carbon, 2.88, 2.93; hydrogen, 0.61, 0.57; oxygen (by difference), 19.54, 19.62. Calculated for lead succinate: lead, 64.10; carbon, 14.86; hydrogen, 1.25; oxygen, 19.79. The compositions of the above precipitates agreed reasonably well with that of the basic lead carbonate, $2PbCO_3 \cdot Pb(OH)_2$, and it was concluded that they were probably formed by the action of carbon dioxide on the lead acetate.

2. One part was tested for the presence of acetonylacetone, or other carbonyl compounds, by the method of Allen[16]; 2,4-dinitrophenylhydrazine was used as the reagent. Negative results were obtained in repeated experiments with both Butyl 1 and Butyl 2.

TABLE III

ISOPRENE DIMERS AND CORRESPONDING DEGRADATION PRODUCTS

Dimer	Structure	Expected degradation products
Myrcene		α-Ketoglutaric acid, formic acid, acetone
Ocimene		Malonic, pyruvic, formic acids; acetone
Allo-ocimene		Oxalic, pyruvic, acetic acids; acetone
Dipentene		Formic acid, 
Possible cyclic dimer		Formic acid, 

3. The third part was analyzed for levulinic acid by the method of Pummerer, Ebermayer, and Gerlach[17], since the Allen method was found in control experiments to be unsatisfactory for this substance. No levulinic acid could be detected in repeated experiments with Butyl 1 and Butyl 2, although control experiments with levulinic acid solutions gave positive reactions with as little as 0.001 gram of the acid.

ANALYSES FOR POSSIBLE PRESENCE OF ISOPRENE DIMERS

According to Whitby and Crozier[18], no open-chain dimers are formed in the polymerization of isoprene in the temperature range 10–145° C. This fact does not preclude the possibility that isoprene dimers may be formed during the low-temperature copolymerization of isoprene with isobutylene, particularly since the reaction environment and the catalysts used differ greatly from the experimental conditions of Whitby and Crozier. Table III lists the various

known or possible pen-chain and cyclic dimers of isoprene, and the corresponding products to be expected upon ozone degradation.

Control experiments were carried out with samples of myrcene and dipentene that had been freshly distilled over phenyl-β-naphthylamine. Samples (0.1 gram) in 150 cc. of purified carbon tetrachloride were ozonized, extracted, and further treated and analyzed in the same manner as described in the preceding section. Precipitates were obtained with lead acetate, and positive tests for carbonyl compounds were found by the Allen method.

The lead salt analyses given above for the aqueous extracts from the polymer experiments indicate that no lead salts corresponding in composition to those that would be obtained from any of the acids listed in Table III were found; nor were any of the carbonyl tests positive, as they were found to have been for myrcene and dipentene. This is considered good evidence for the absence of any of the known isoprene dimers in the polymers investigated.

CONCLUSIONS

By means of ozone degradation experiments it has been shown that the isoprene units in copolymers of isoprene and isobutylene unite in the 1,4 positions. This conclusion is based on negative evidence. Since no evidence was found that would indicate a tendency for the isoprene units to occur in sequences, it is concluded that one isoprene unit cannot exert any directing influence on another, as far as their relative positions along the polymer chain are concerned. The existence of such an influence would necessitate the assumption of unprecedented long-range forces. Hence, the isoprene units must enter the chain in a random manner.

ACKNOWLEDGMENT

The writer is indebted to (Mrs.) M. D. Robbins for carrying out much of the experimental work, and to Paul J. Flory for the benefit of valuable discussions.

REFERENCES

[1] Thomas, Lighbown, Sparks, Frolich and Murphree, *Ind. Eng. Chem.* **32**, 1283 (1940); Thomas, Sparks, Frolich, Otto and Mueller-Cunradi, *J. Am. Chem. Soc.* **62**, 276 (1940); Thomas and Sparks, Australian patent 112,875 (1941).
[2] Pummerer, Matthäus and Socias-Viñals, *Ber.* **69**, 170 (1936); Aleekseeva, *J. Gen. Chem.* (U.S.S.R.) **9**, 1426 (1939); **11**, 353 (1941); Hill, Lewis and Simonsen, *Trans. Faraday Soc.* **35**, 1067, 1073 (1939); Alekseeva and Belitskaya, *J. Gen. Chem.* (U.S.S.R.) **11**, 358 (1941).
[3] Fuller, Frosch and Pape, *J. Am. Chem. Soc.* **62**, 1905 (1940); Thomas, Sparks, Frolich, Otto and Mueller-Cunradi, *J. Am. Chem. Soc.* **62**, 276 (1940).
[4] Fuller, C. S., private communication; Rehner, J., Jr., unpublished results.
[5] Fuller, Frosch and Pape, *J. Am. Chem. Soc.* **62**, 1905 (1940).
[6] Rehner, J., Jr., unpublished results.
[7] Flory, *J. Am. Chem. Soc.* **65**, 372 (1943).
[8] Weinberg, *Ind. Eng. Chem. Anal. Ed.* **3**, 365 (1931).
[9] Weygand, "Organisch-chemische Experimentierkunst", Barth, Leipzig, **1938**, p. 125.
[10] Erdmann, *Ann.* **362**, 148 (1908); Harries, "Untersuchungen über die natürlichen und künstlichen Kautschukarten", Julius Springer, Berlin, **1919**, p. 51.
[11] Döbereiner, *Ann.* **3**, 142 (1832); Portes and Ruyssen, *Compt. rend.* **82**, 1504 (1876); *J. Chem. Soc.* **2**, 663 (1876); Auerbach and Plüddeman, *Arb Kaiserl. Gesundh.* **30**, 178 (1910).
[12] Fenton and Sisson, *Proc. Cambridge Phil. Soc.* **14**, 385 (1908).
[13] Fieder, *Arch. Pharm.* **245**, 25 (1907).
[14] Scala, *Gazz. chim. ital.* **20**, 393 (1890).
[15] Rose, *Pogg. Ann.* **106**, 500 (1859); Mellor, "Comprehensive Treatise on Inorganic and Theoretical Chemistry", London, Longmans, Green & Co., **1923**, Vol. IV, p. 827.
[16] Allen, *J. Am. Chem. Soc.* **52**, 2955 (1930).
[17] Pummerer, *Kolloid-Z.* **53**, 75 (1930); RUBBER CHEM. TECH. **4**, 206 (1931); Pummerer, Ebermayer and Gerlach, *Ber.* **64**, 804 (1931); RUBBER CHEM. TECH. **4**, 381 (1931).
[18] Whitby and Crozier, *Canadian J. Research* **6**, 203 (1932).

MACROMOLECULAR COMPOUNDS

CCCII. POLYMERIZATION OF ACRYLONITRILE. POLYACRYLONITRILE *

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Products obtained by the polymerization of vinyl compounds and acryl compounds are among the most important of synthetic organic materials. Each of these unsaturated compounds imparts special properties to the simple polymers and mixed polymers prepared from them, and it is because of these special properties that the polymers have found such wide application. Acrylonitrile, for example, is used technically on a large scale, particularly as a component in mixed polymerizations, and it imparts characteristic properties to the mixed polymers, *e.g.*, resistance to organic solvents[1]. In contrast to most other polyvinyl and polyacryl compounds, polyacrylonitrile is insoluble in organic solvents, and because of the unusual behavior of this polymer, it seemed of interest to study the polymerization of acrylonitrile and some of the products of its polymerization.

In the polymerization of vinyl compounds, either soluble or insoluble polymers are obtained, depending on the type of monomer and the choice of operating conditions. Styrene, vinyl acetate, methacrylonitrile, and acrylic and methacrylic esters of monohydroxy alcohols yield soluble polymers. On the contrary, when divinylbenzene and likewise acrylonitrile are polymerized, insoluble polymers are obtained. Vinylmethyl ketone, butadiene and other compounds yield either soluble or insoluble products, depending on the experimental conditions.

The chemical constitution of the soluble polymers is now understood in a general way as a result chiefly of the investigations of Staudinger[2] and his school of investigators. These substances are constituted of macromolecules in which a large number of carbon atoms are united by primary valences to carbon chains carrying long, side groups. It is generally believed today that the macromolecules of polystyrene[3] have more or less extensive branchings, whereas the structure of the macromolecules of polyvinyl acetate and polymethyl methacrylate is not even yet definitely settled.

Divinyl compounds yield chiefly insoluble polymers, and at least in this case the reason for their insolubility is understood[4]. Whereas monovinyl compounds polymerize to soluble, linear macromolecules (providing complications such as the branching reaction already mentioned are disregarded), divinyl compounds yield in most cases products which have a network structure and which, therefore, are insoluble. Polymers with network structures of this kind are composed of three-dimensional macromolecules, and are, for example, formed from *p*-divinylbenzene[4], divinyl ether[5], hydroquinone diacrylate[6], and butadiene. Investigation of these polymers is very difficult or

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even impossible because of their insolubility; for all methods of measuring the size and shape of macromolecules are based on measurements of substances in solution.

Whereas a reason can be found for the insolubility of polymers from divinyl compounds, the insolubility of polyacrylonitriles is not so easily explained. Based on reliable observations on the polymerization of unsaturated compounds, this type of polymerization leads to chain molecules of the following character[7]:

(1) ····—CH_2—CH(R)—CH_2—CH(R)—CH_2—CH(R)—CH_2—CH(R)—····

(2) ····—CH_2—CH(R)—CH(R)—CH_2—CH_2—CH(R)—CH(R)—CH_2—····

(3) ····—CH_2—CH(R)—CH_2—CH(R)—CH_2—CH(R)—CH(R)—CH_2—····

Investigations of numerous polymeric vinyl compounds[8], including polystyrene, polyvinyl acetate, polyvinyl alcohol and polyvinyl chloride, point to structure (1) as that characteristic of these polymers. On the other hand, polymeric acryl and methacryl compounds[9] have structure (2), or perhaps even structure (3). It is probable that the polymer of acrylonitrile has this same structure, although structure (1) should not be considered out of the question altogether. It would be expected that linear chain molecules with lateral cyano groups, such as are shown in structures (1), (2) and (3), would be soluble in various organic solvents. However, polyacrylonitrile is wholly insoluble, and up to the present time no solvent for this polymer has been found[10].

It was the object of the present work to study the polymerization of acrylonitrile, the products of this polymerization, and the reasons for the insolubility of the polymers. Although it was not possible to accomplish everything desired, numerous observations were made with regard to the polymerization of acrylonitrile and to the products of this polymerization, and these will be described in the following pages.

THERMAL AND CATALYTIC POLYMERIZATION OF ACRYLONITRILE

SOLUTION POLYMERIZATION

First of all, a series of experiments was carried out on the polymerization of pure, monomeric acrylonitrile[11], the object of which was to obtain soluble polymers. It was expected that a study of soluble polymers of this type would make it possible to draw conclusions as to the constitution of insoluble polymers. Accordingly the conditions of polymerization were studied with great care.

It was first proved that polymerization cannot be brought about with the aid of heat alone. Temperatures as high as 160° C were tried, without any appreciable polymerization taking place. On the contrary, styrene can be polymerized by heating, although far more slowly than by the addition of a catalyst. Acrylonitrile which has not been purified very carefully polymerizes when heated, and even changes slowly at room temperature on long standing.

The influence of catalysts on polymerization was then studied. Most of the experiments were carried out with benzoyl peroxide. With tetralin perox-

ide the phenomena were essentially the same; polymerization was slower, and in general tetralin peroxide was found to be a less active accelerator than benzoyl peroxide. Concentrations of catalyst from 0.001 to 5 per cent were tried, and temperatures of polymerization from room temperature to 100° C. As with other unsaturated compounds, the velocity of polymerization increased with increase in temperature and with increase in the concentration of catalyst.

In the catalytic polymerization of acrylonitrile with benzoyl peroxide, a well defined temperature range was observed, below which polymerization was extremely slow. This temperature threshold was approximately 30° C. Below this temperature, the only effect was a yellow coloration of the acrylonitrile, which otherwise remained quite clear and mobile. With a rise of temperature only 5° C above this point, polymerization set in. The liquid first became turbid, a white flocculent precipitate formed, and the polymer continued to precipitate until the polymerization reaction was completed. The course of the reaction is thus the same as in all polymerization reactions in which the polymers are insoluble in their monomers[12].

The velocity of polymerization was not measured quantitatively, but certain data which were obtained will serve as an indication of the rate of the reaction. Polymerization of 1 gram of pure acrylonitrile with 1 per cent of benzoyl peroxide was complete in approximately 20 minutes at 100° C. But even after heating for several days at 100° C, especially with larger quantities of ingredients, monomeric acrylonitrile was still present in the mixture. In some cases as much as 40 per cent of the acrylonitrile remained unpolymerized, and this unreacted acrylonitrile did not decrease even on longer heating. On the other hand, no benzoyl peroxide could be detected after the polymerization reaction had become inappreciable, and therefore it is wholly consumed by the polymerization reaction or by side reactions. With high concentrations of catalyst, *e.g.*, 5 per cent, and at elevated temperatures, *e.g.*, 90° C, the polymerization reaction is extremely energetic, sometimes leading to violent explosions[13].

With acrylonitrile it is not possible to obtain soluble polymers by using high concentrations of catalysts, as can be done with other vinyl compounds and acryl compounds, which give products of low states of polymerization that dissolve readily in solvents and give solutions of low viscosity.

The polyacrylonitriles which were obtained under widely different conditions of temperature and concentration of catalyst did not differ particularly in appearance, despite the fact that their rates of polymerization differed greatly. All polymeric products obtained by block polymerization were insoluble in all organic solvents which were tested.

Nor did polymerization in solution, *e.g.*, in toluene, benzonitrile, acetone, acetonitrile and other solvents, yield soluble polymers. In all cases the polymers were precipitated as insoluble products, and only a very small fraction remained in solution and could be precipitated visibly as a slight turbidity by certain agents, *e.g.*, methanol. When they were still moist, it was found possible to redissolve these precipitates partially. However, after the precipitates had been separated and dried, the products were completely insoluble. Polyacrylonitriles are soluble in concentrated sulfuric acid, with partial saponification.

PROPERTIES OF POLYACRYLONITRILES

The polyacrylonitriles obtained were white or yellow, crumbly or brittle masses, which could easily be pulverized. They had the appearance of hemi-

colloidal linear colloids[14], *e.g.*, low-polymeric polystyrenes. The polymers were not thermoplastic, and they had no definite softening points. Up to 300° C there was no appreciable change; at approximately 350° C decomposition set in. This behavior is in sharp contrast to that of other polyvinyl compounds, *e.g.*, polystyrene, polyvinyl acetate and polymethacrylic esters, which show low softening points. There seems to be a general relation between the softening point and solubility of high-molecular compounds, *viz.*, with increase in the softening temperature, the number of solvents in which a compound is soluble decreases.

With respect to insolubility in solvents, it is an interesting question whether polyacrylonitriles crystallize. A roentgenographic examination[15] showed not only a broad band, but also interferences which indicated the presence of crystalline components.

As an aid to characterizing the polyacrylonitriles under investigation, an elementary analysis of a polymer prepared with 1 per cent of benzoyl peroxide is given below. Since these polymeric products could not be purified, the benzoyl peroxide content must be taken into account.

	99%	C_3H_3N + 1%	$C_{14}H_{10}O_4$
Calculated	C 67.98	H 5.64	N 26.16
Found	C 67.70	H 5.92	N 25.66

The low nitrogen value probably cannot be attributed to an impurity in the monomeric acrylonitrile, for an elementary analysis of this latter showed normal values (see Reference 11). Rather it should be attributed to splitting off of hydrogen cyanide, which takes place during polymerization. This evolution of hydrogen cyanide, which is analogous to the splitting off of hydrogen chloride in the polymerization of vinyl chloride[16], is discussed in more detail in the following section.

THE FORMATION OF HYDROGEN CYANIDE IN THE POLYMERIZATION OF ACRYLONITRILE WITH BENZOYL PEROXIDE AS CATALYST

In the polymerization of acrylonitrile with benzoyl peroxide, it was observed that, at the beginning of polymerization, the acrylonitrile turns pale yellow, and an intense odor of hydrogen cyanide is evolved. This hydrogen cyanide was identified in the form of silver cyanide and as Prussian blue. It was especially easy to detect hydrogen cyanide when little or no polymer had yet been formed, *e.g.*, when the reaction was carried out below 30° C. The cause of the evolution of hydrogen cyanide is to be sought in some kind of action by benzoyl peroxide. Without the latter no hydrogen cyanide could be detected at low temperatures. Slight thermal decomposition of acrylonitrile, with formation of hydrogen cyanide, was found to take place on prolonged heating (60 hours) and at essentially higher temperatures (100° C). Neither decomposition products of benzoyl peroxide, *e.g.*, benzoic acid, nor a trace of moisture can be held responsible for the formation of hydrogen cyanide.

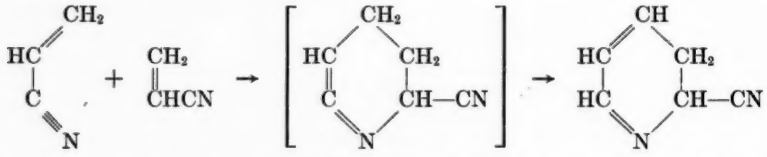
It was found also that hydrogen cyanide is split off from other nitriles under the influence of benzoyl peroxide (1 per cent), *e.g.*, benzyl cyanide evolved quite an appreciable amount, acetonitrile evolved much less. On the contrary, under the same conditions, neither benzonitrile nor cinnamonitrile evolved any detectable amounts of hydrogen cyanide. In the case of cinnamonitrile, this is particularly surprising, for this nitrile can be regarded as a derivative of acrylonitrile. Methacrylonitrile polymerizes in the presence of

benzoyl peroxide, but in this case no hydrogen cyanide could be detected to the point of the reaction at which polymerization had progressed, with 1–5 per cent of benzoyl peroxide, to the formation of solid, block polymers. In this case the use of a high vacuum, the presence of air, or carrying out the polymerization in purified nitrogen, had no influence on the results. However, when the polymerization reaction was interrupted before completion, a distinct positive test for hydrogen cyanide was obtained by extracting the rather viscous semipolymerized methacrylonitrile[17] with very dilute sodium hydroxide. The same result was obtained when polymerization was carried out in toluene solution, in which solvent the polymer is insoluble and from which it therefore precipitates.

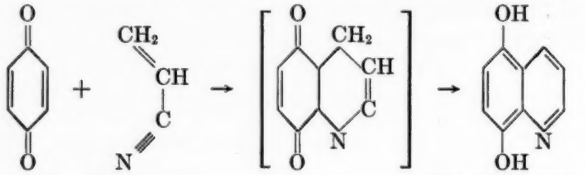
Further experiments were carried out to ascertain whether other decomposition products of acrylonitrile in addition to hydrogen cyanide are formed in appreciable amounts. Three possibilities were visualized: (1) the decomposition of acrylonitrile into hydrogen cyanide and acetylene[18]; (2) a dimerization reaction, and (3) a transformation of monomeric acrylonitrile with benzoyl peroxide.

Reaction (1).—All experiments to detect acetylene in addition to hydrogen cyanide as a decomposition product of acrylonitrile gave negative results. However, the possibility should not be overlooked that a mixed polymerization of acrylonitrile with acetylene is the cause of the insolubility of the polyacrylonitrile.

Reaction (2).—With many unsaturated compounds, dimerization takes place as a concurrent reaction to chain polymerization. Thus, butadiene forms vinylcyclohexene[19]; acrolein[20], crotonaldehyde[21] and methylvinylketone[22] form pyran derivatives. A corresponding reaction of acrylonitrile would proceed as follows:



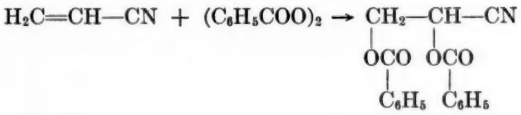
The nitrile of dihydropicolinic acid formed in this way might be stabilized by the splitting off of hydrogen cyanide and formation of pyridine. Nevertheless, no pyridine or other basic reaction product could in any case be detected in acrylonitrile which had been subjected to a wide variety of conditions, both of temperature and of catalyst, even with the most carefully chosen methods of identification. Only in the distillation residues of technical acrylonitrile was a positive test for pyridine obtained. Dimerization of the character shown in the scheme above could not, therefore, be confirmed, and it cannot account for the formation of hydrogen cyanide. If acrylonitrile is capable of reacting as a diene and thus enters into diene syntheses, it should react also with dienophilic compounds such as quinone[23], in the following way:



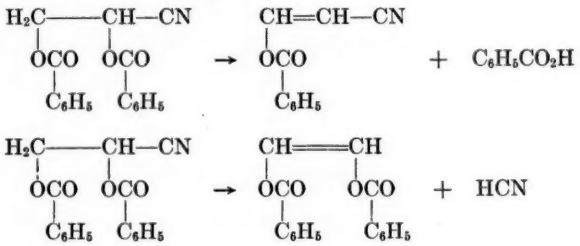
dihydroxyquinoline

Actually, however, even under the most varied conditions of temperature, concentration and proportions of benzoyl peroxide, no transformation product of acrylonitrile and quinone could be identified.

Reaction (3).—It is known that benzoyl peroxide is capable of adding on to double bonds[24], *e.g.*, to dinaphthylene dioxide[25] and to rubber[26]. With most unsaturated compounds, the detection of such an addition is rendered extraordinarily difficult because of the accompanying chain polymerization. In the case of acrylonitrile, the addition of benzoyl peroxide can be represented in the following way:



This addition product may decompose, with liberation either of benzoic acid[27] or of hydrogen cyanide:



In all probability it is in these secondary reactions that an explanation is to be found for the formation of hydrogen cyanide in chain polymerizations catalyzed by benzoyl peroxide.

MIXED POLYMERIZATION OF VINYL COMPOUNDS WITH HYDROGEN CYANIDE

The formation of hydrogen cyanide in the catalytic polymerization of acrylonitrile pointed to a possible explanation of the insolubility of polyacrylonitrile, *viz.*, that acrylonitrile forms a mixed polymer and thereby a molecule with a network structure. If this assumption is correct, hydrogen cyanide and other unsaturated compounds as well should form insoluble polymers with limited tendency to swell. However, it was found that when 0.5 to 5 per cent of anhydrous hydrogen cyanide was added to styrene, to vinyl

TABLE 1

POLYMERIZATION OF STYRENE, VINYL ACETATE AND POLYMETHYL METHACRYLATE WITH THE ADDITION OF 5 PER CENT OF ANHYDROUS HYDROGEN CYANIDE AND 1 PER CENT OF BENZOYL PEROXIDE

Time of polymerization = 120 hours
Temperature = 50° C

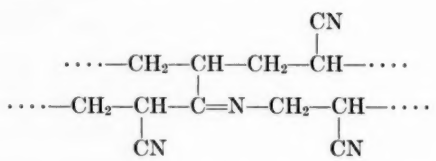
Product	Percentage HCN
Polystyrene	0.33
Polyvinyl acetate	0.97
Polymethyl methacrylate	1.35

acetate and to polymethyl methacrylate, only soluble polymers were obtained[27], and these latter retained a strong odor of hydrogen cyanide. After the polymers had been freed of monomeric hydrogen cyanide in a high vacuum, a nitrogen determination indicated only very small percentages of hydrogen cyanide (see Table 1).

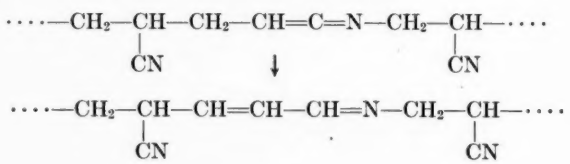
Mixed polymerization of vinyl compounds and hydrogen cyanide takes place, therefore, to only a slight extent, if at all, and it does not have any effect on the solubility of the polymers. Methacrylonitrile, which likewise splits off hydrogen cyanide under the influence of benzoyl peroxide, gives soluble polymers. Consequently with acrylonitrile as well, hydrogen cyanide cannot be the cause of the reaction which forms a network structure and thereby renders the polymers insoluble.

THE POSSIBILITY OF THE FORMATION OF A NETWORK STRUCTURE BY THE INCLUSION OF CYANO GROUPS IN THE CHAIN MOLECULES OF POLYACRYLONITRILE

Consideration must still be given to the inclusion of cyano groups in the chain molecules as the cause of the insolubility of polyacrylonitrile. It is easy to visualize that in this case bridge bonds and hence a network structure might be formed, thus:



It is conceivable also that acrylonitrile, although incapable of undergoing a diene synthesis, can react in the sense of a 1,4-polymerization, in which case the following molecular grouping would be formed:



The double bonds in the chain which are formed in this reaction may in turn react to form a network structure. In both cases the grouping present in a Schiff base would be expected.

A further possible way of forming a network structure which should be considered is the formation of a triazine ring from three cyano groups. In this case it is immaterial, as far as the final result is concerned, whether the triazine ring is formed from the monomeric acrylonitrile (trivinyltriazine) or only from the cyano groups of polymeric molecules.

The formation of a network structure by cyano groups is very difficult to understand. Both Schiff bases and triazines are stable toward alkalies, and therefore it might be expected that the alkaline saponification of polyacrylonitrile would aid in solving the problem.

SAPONIFICATION OF POLYACRYLONITRILE

When finely powdered polyacrylonitrile is heated with concentrated (40 per cent) sodium hydroxide solution, the suspended material becomes an intense red color after a certain length of time, and gradually passes into solution, with disappearance of the red color. Quantitative determination of the ammonia which is formed in this reaction gives values which are always only 94–95 per cent of the theoretical quantities. It is evident, therefore, that there is nitrogen present which is saponified only with difficulty by alkalies. Since, however, the sodium polyacrylate which is formed by the saponification is soluble, it is impossible to draw any conclusions as to the positions in the molecules where cyano groups take part in the formation of the network structure. If it is not assumed that some of the nitrile groups or acid amide groups formed from these nitrile groups are particularly difficult to saponify, then the assumption is probably correct that a small proportion of the nitrile groups take part in the polymerization reaction. Moreover, a comparison with methacrylonitrile leads to the same conclusion, *i.e.*, polymethacrylonitrile

TABLE 2

SPECIFIC VISCOSITY, HYDROGEN-ION ACTIVITY AND MACROMOLECULAR FACTOR OF POLYACRYLIC ACIDS OBTAINED BY SAPONIFICATION OF POLYACRYLONITRILE

c_g	η_{sp}/c_g	$h \times 10^4$	$(\eta_{sp}/c_g)_m$
0.0035	44.2	1.45	1.03
0.0058	31.9	2.00	1.02
0.0095	21.4	2.91	0.99
0.024	15.1	5.02	1.20
0.038	10.0	6.73	1.06
0.066	9.6	9.51	1.44
0.101	10.0	13.7	2.06
0.183	9.8	19.9	3.08
0.306	9.3	27.6	4.06
0.510	10.0	40.2	6.37

likewise contains difficultly saponifiable nitrogen, yet is soluble in various organic solvents, and therefore certainly does not contain even a partial network structure.

For all these reasons, the assumption that polyacrylonitrile is insoluble because of its molecules forming in part a network structure becomes improbable. Rather it must be assumed that the cyano groups show high molecular cohesion, as do the hydroxyl groups of cellulose, so that organic solvents are not able to overcome this cohesion. If this is so, it is of course difficult to explain why polymethacrylonitrile is soluble in various organic solvents. It is perhaps to be explained by the numerous methyl groups, which for purely steric reasons cause a loosening of the structure of the polyacrylonitrile chain[29].

The polyacrylic acid which is formed by saponification can be recovered by mild acidification, dialysis, and evaporation of the aqueous solution. The elemental analysis of a pure product was as follows:

$C_3H_4O_2$	Calculated	C 50.00	H 5.56	N —
	Found	50.13	6.45	0.17

The saponification product is therefore a practically pure polyacrylic acid. Its degree of polymerization can be estimated in an approximate way by measuring the viscosities of aqueous solutions.

When the specific viscosities $\eta sp/c_g$ of aqueous solutions of polyacrylic acids are plotted against the base molar concentration c_g, characteristic curves are obtained[30]. The specific viscosities of colloids with heteropolar molecules can be resolved into an ionic factor and a macromolecular factor[31]. The ionic viscosity factors do not depend on the concentration. Since the ionic viscosity factors of polyacrylic acids are known[31], the macromolecular factors can be calculated, and from these the average molecular weight and average degree of polymerization can be estimated. Table 2 shows the specific viscosities, the hydrogen-ion activities and the calculated macromolecular factors of the specific viscosity of polyacrylic acids obtained by saponification of a polyacrylonitrile. The increase constant K_{St} is found to be 0.46, the average degree of polymerization approximately 270. This degree of polymerization should be regarded as merely the minimum value, since the decomposition of the original polyacrylonitrile probably depends on the conditions of saponification. In any event, the saponification of polyacrylonitrile and the determination of the degree of polymerization of the saponification product furnish proof of the macromolecular character of polyacrylonitrile to an extent which is not possible by other means on account of its insolubility.

THERMAL DECOMPOSITION OF POLYACRYLONITRILE

One of the methods which is widely used in attempts to explain the structure of polymeric substances is thermal decomposition[32]. Polyacrylonitrile has a high heat resistance, and up to 300° C it undergoes no appreciable change. Without passing through any definite softening point[33], it decomposes at a still higher temperature, with distillation of a small proportion (15 per cent) and carbonization of the distillation residue. The volatile components were separated into three fractions. They contained nitrogen and were basic, but were not identified further, because of insufficient quantities. Table 3 gives some data on these three fractions.

TABLE 3

VOLATILE FRACTIONS IN THE THERMAL DECOMPOSITION OF POLYACRYLONITRILE

Fraction	Boiling range	Solubility in water	Odor
I	50–60° C	miscible	ammoniacal
II	85–95° C	miscible	aliphatic amines
III	155–160° C at 13 mm. Hg	difficultly soluble	—

It is noteworthy that, in the thermal decomposition of polyacrylonitrile, there is no depolymerization of the polyacrylonitrile to monomeric acrylonitrile, although at the temperatures used monomeric acrylonitrile is fairly stable. In contrast to this, in the thermal decomposition of polystyrene[34], monomeric styrene is formed among other products; rubber yields isoprene; and polymethyl methacrylate depolymerizes almost quantitatively to methyl methacrylate[35].

REFERENCES

[1] For example, Perbunan of the I. G. Farbenindustrie A.-G.
[2] Staudinger, "Die hochmolekularen organischen Verbindungen", Julius Springer, Berlin, **1932**; "Organische Kolloidchemie", Vieweg & Sohn, Braunschweig, 2nd Ed., **1941**.
[3] Staudinger and Schulz, **68**, 2334 (1935).
[4] Staudinger and Heuer, *Ber.* **67**, 1164 (1934); Staudinger and Husemann, *Ber.* **68**, 1618 (1935).
[5] Blaikie and Crozier, *Ind. Eng. Chem.* **28**, 1158 (1936).
[6] Kern, *Kunststoffe* **28**, 257 (1938).
[7] Kern and Houwink, "Chemie und Technologie der Kunststoffe", 2nd Ed., Vol. I, Akad. Verl.-Ges., Leipzig, **1942**, p. 25.

[8] Staudinger, Frey and Starck, *Ber.* **60**, 1782 (1927); Staudinger and Schwalbach, *Ann.* **488**, 8 (1931); Staudinger and Steinhofer, *Ann.* **517**, 35 (1935); Marvel and Denoon, *J. Am. Chem. Soc.* **60**, 1045 (1938); Marvel, Sample and Roy, *J. Am. Chem. Soc.* **61**, 3241 (1939).

[9] Marvel and Cowan, *J. Am. Chem. Soc.* **61**, 3156 (1939); Marvel and Levesque, *J. Am. Chem. Soc.* **61**, 3244 (1939).

[10] After the conclusion of this work in the middle of 1940, there came to the attention of the authors German patent 681,527, in which the solubility of polyacrylonitrile in aqueous concentrated solutions of inorganic salts, particularly lithium bromide, sodium thiocyanate and zinc chloride is recorded. This patent gives a new insight into the insolubility of polyacrylonitrile.

[11] The starting material for the laboratory preparation is ethylenecyanhydrin, which is dehydrated by phosphorus pentoxide (cf. Moureu and Brown, *Bull. soc. chim.* [4] **27**, 901 (1920). By repeated fractionations over phosphorus pentoxide, acrylonitrile was obtained in pure form. In addition to this pure product, there was available for the work a technical grade of acrylonitrile of the I. G. Farbenindustrie A.-G., which likewise was purified by repeated distillation over phosphorus pentoxide. The boiling point of pure acrylonitrile is 75–76° C (uncorrected). The product showed an analysis:

Found	C 67.92	H 5.66	N 26.42
Calculated	C 67.97	H 6.02	N 26.34

The authors wish to express their thanks to the management of the I. G. Farbenindustrie A.-G., Werk Höchst, for the contribution of technical acrylonitrile.

[12] In the same way, polycyclopentadiene is insoluble in cyclopentadiene, and polyacrylic acid is insoluble in acrylic acid (cf. Staudinger and Urech, *Helv. Chim. Acta* **12**, 1107 (1929); Staudinger, *Ber.* **53**, 1073 (1920).

[13] In the case of methyl methacrylate, the explosive nature of the polymerization has been thoroughly studied by Schulz and Blaschke (cf. *Z. Elektrochem. angew. physik. Chem.* **47**, 749 (1941).

[14] Staudinger, "Organische Kolloidchemie", Vieweg und Sohn, Braunschweig, 2nd Ed., **1941**, p. 125.

[15] The authors wish to show their appreciation to Dr. Plötze of the Physical Institute of the University of Freiburg/Br. for preparing the Debye-Scherrer diagrams.

[16] Staudinger and Schneiders, *Ann.* **541**, 151 (1939).

[17] The monomeric methacrylonitrile which was used contained no trace of hydrogen cyanide.

[18] Acrylonitrile is formed by the reaction of acetylene with hydrogen cyanide (cf. German patent 559,734; *Chem. Zentr.* **1932**, II, 3305).

[19] Hofmann and Tank, *Z. angew. Chem.* **25**, 1465 (1912); Alder and Rickert, *Ber.* **71**, 373 (1938).

[20] Alder and Ruden, *Ber.* **74**, 920 (1941).

[21] Alder, Offermans and Ruden, *Ber.* **74**, 926 (1941).

[22] Alder, Offermans and Ruden, *Ber.* **74**, 905 (1941).

[23] Maleic anhydride is not suitable, because it forms mixed polymers with acrylonitrile.

[24] The splitting off of benzoic acid in the reaction of benzoyl peroxide with unsaturated compounds has frequently been observed (cf. Rieche, "Die Bedeutung der organischen Peroxide für die chemische Wissenschaft und Technik", Verlag Enke, Stuttgart, **1936**, pp. 14 and 69.

[25] Pummerer and collaborators, *Ann.* **503**, 40 (1933).

[26] Bock, *Kautschuk* **7**, 224 (1931).

[27] In the case of styrene, the formation of benzoic acid when the polymerization is catalyzed by benzoyl peroxide has been conclusively demonstrated (unpublished experiments of Kern and Kämmerer).

[28] The rate of polymerization is greatly diminished by hydrogen cyanide.

[29] With regard to the influence of methyl groups on the solubility of paraffins with high molecular weights, see Staudinger and Leupold, *Helv. Chim. Acta* **15**, 221 (1932).

[30] Staudinger and Trommsdorff, in Staudinger, "Die hochmolekularen organischen Verbindungen", Julius Springer, Berlin, **1932**, p. 333; Kren, *Z. physik. Chem.* [A] **181**, 283 (1938).

[31] Kern, *Z. physik. Chem.* [A] **181**, 283 (1938).

[32] Compare, for example, the thermal decomposition of rubber (cf. Staudinger and Geiger, *Helv. Chim. Acta* **9**, 549 (1926)) with that of polystyrene (cf. Staudinger and Steinhofer, *Ann.* **517**, 35 (1935)).

[33] In contrast to insoluble polyacrylonitrile, soluble polymethacrylonitrile has a softening point of approximately 115° C.

[34] Staudinger and Steinhofer, *Ann.* **517**, 35 (1935).

[35] Staudinger and Werth, *J. prakt. Chem.* [2] **155**, 286 (1940).

POSITION OF THE RUBBERLIKE STATE ON THE PLASTIC-ELASTIC SCALE *

J. M. Buist and R. C. Seymour

Introduction.—The rubberlike state is characteristic of a particular physical condition of matter, rather than of particular chemical structures. This has been proved by the development of synthetic materials which exhibit rubberlike properties, but which differ considerably from natural rubber in chemical composition. It is now clear that rubberlike properties are shown by materials composed of long-chain molecules, possessing internal flexibility which has been attributed to a certain degree of freedom of rotation about interchain bonds, *e.g.*, carbon-carbon linkages in polyhydrocarbons, sulfur-sulfur linkages in elastic sulfur, although this interpretation has been doubted by some authors.[1]

The accepted explanation of the retractive force in stretched rubber, on this kinetic-statistical basis, is that the stretched-out chains tend to return to the coiled, unstretched state. This is the more probable on energetic considerations.

The characteristics of the rubberlike state can therefore be interpreted on a physical basis, and Meyer[2] has described the properties of rubberlike materials as being solid in one dimension and liquid in the other two. Solid properties arise from the linkage of an individual atom to its two neighbors in the chain by covalent bonds, whereas liquid properties are determined by the field of van der Waals's forces of its neighbors in the other two dimensions. Thus it is to be expected that the state of aggregation of such substances is intermediate between the liquid and solid states, and that rubberlike properties possess mixed characteristics of true elasticity and true fluidity.

For materials such as rubbers, stress is not a single valued function of strain. The mechanical characteristics, *e.g.*, modulus of elasticity and coefficient of viscosity, of these materials, are not constants, but depend on the time and rate of deformation employed in their measurement. Thus, such constants lose their significance, and it is necessary to find new characteristics, which do not depend on the time and manner of deformation.

These characteristics can be described in two ways, either mathematically, by a general equation,[3] which contains as special solutions, the conditions of true elasticity and fluidity, or graphically, by a plastic-elastic scale.[4]

THEORETICAL

The elasticity of rubberlike materials differs from true elasticity by reason of its complex dependence on temperature and frequency of application of stress. Under rapidly alternating stresses, or at low temperatures, the behavior of rubber approximates that of a rigid elastic solid, whereas under constant loads applied over a long period, or at sufficiently high temperatures, flow can occur, even in vulcanized rubber. In general, the deformation of rubber under stress is a complex summation of truly elastic, highly elastic and viscous

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deformations. The dependence of the total deformation on time and temperature is associated principally with the highly elastic component.

In determining the laws which govern the deformation of such materials, two general methods are available. First, the analytical approach, by which the total deformation is divided into its components, and each is studied separately. This method lends itself to great clarity in formulating the problem, but fails, if no attempt is made at synthesis, to account for the interaction between individual components. Secondly, the integrative approach, much used in industry, in which empirical relationships are deduced from observation of the total deformation.

It is useful to consider the application of these methods, to show that each arrives at similar conclusions.

The deformation of rubberlike materials.—An example of one type of analytical method has been developed by Alexandrov and Lazukrin[5] from the Mark-Kuhn theory[6] of the structure of rubberlike materials. These authors have proposed that the total elastic deformation produced in a polymer under a given stress be divided into deformations, differing in mechanism:

$$D = D_{oe} + D_{He}$$

where D_{oe} is the truly elastic deformation, attained instantaneously, and associated with the positional separation of chain segments, against the influence of van der Waals's forces. D_{He}, the highly elastic component of deformation, is due to changes in the freedom of internal rotation, *i.e.*, does not affect the mean distance between chains, and clearly depend on time. As a first approximation:

$$D_{He(t)} = D_{He\infty}(1 - e^{-t/\tau})$$

where t is the time interval between the instant at which the stress is applied and the instant at which deformation is observed, τ being the time required for the chains to orient themselves under stress. This highly elastic deformation has been interpreted as a relaxation process,[7] and the extent of the total deformation thus depends on the ratio of the time of application of stress, to the orientation time τ.

If $t < \tau$, highly elastic deformation is not fully developed, and the material shows a closer approximation to true elasticity, its behavior approaching that of a rigid elastic solid. If $t > \tau$, time is allowed for highly elastic deformation to develop fully, and the material shows typically highly elastic deformation.

In the region, $t \leqq \tau$, the dependence of the extent of deformation on the time t is most marked. This leads to an interesting explanation of the discrepancy between behavior in laboratory tests and in service. The deformation of rubber under service conditions can only be reproduced in laboratory testing when the relationship of t and τ is in each case identical. Furthermore, the maximum discrimination in the dynamic testing of synthetic rubbers would be obtained only by the use of stress-frequencies chosen to be of the same order as the orientation times.

Gurevitch and Kobeko[8] have similarly pointed out the incorrect conceptions, held by some workers, of the behavior of highly elastic materials under working conditions, due to ignoring the effect of time and temperature on deformation.

The analysis of deformation has been extended by Eley,[9] who treats highly elastic orientation as a unimolecular rate process, and by the introduction of

a term for viscous flow, derives a complete deformation equation:

$$D = D_{oe} + D_{He} + D_{visc}$$

i.e.,

$$D(t, T, S) = \frac{S}{E_{oe}} + \frac{S}{E_{He\infty}}(1 - e^{-t/\tau}) + \frac{tS}{\eta}$$

where S is the applied stress, E_{oe} and $E_{He\infty}$ are elastic moduli. In relation to this view, it must be observed that a similar treatment[10] of viscous flow as a unimolecular rate process has led to useful developments.

The properties of rubberlike materials depend on time and temperature, and the effects of these two factors are obviously related. Thus under high frequency alternating stresses, or at low temperatures, rubber is not highly elastic, but at very high temperatures or under stresses acting over long periods, viscous flow can be observed; there appears to be an inverse relationship between time t and temperature T. The theoretical explanation of this relation can be shown in the following way.

Orientation of the chains can be treated as a transition from a state A to a state A', overcoming a potential barrier U. The rate at which this orientation proceeds is proportional to the probability W that a chain can undergo such an arrangement:[11]

$$W = Ce^{-u/kT}$$

where k is the Boltzmann constant, C is a coefficient, and T is the absolute temperature. Thus

$$\tau = \frac{A}{e^{-u/kT}} = Ae^{u/kT} \text{ where } A \text{ is a constant.}$$

If τ is treated as a unimolecular rate constant:[12]

$$\tau = \frac{h}{kT} e^{\Delta G/RT} \tag{1}$$

where ΔG is the Gibbs free energy of activation for orientation, h is Planck's constant, and R is the gas constant.
If the condition $t \cong \tau$ is satisfied, we see that the relation:

$$t = \frac{h}{kT} e^{\Delta G/RT} \tag{2}$$

predicts the inverse effects of time and temperature on deformation.

If it is assumed that a particular value of τ characterizes the behavior of natural rubber, the synthetic materials can then be placed[13] in relation to natural rubber according to the temperature range T_E over which this τ value is achieved. T_E is much less than room temperature in the case of natural rubber, Neoprene and polyisobutylene, and these materials show rubberlike properties at normal temperatures. In all cases the general character of the relationship between T_E and τ is similar, for example, methyl methacrylate is solid at room temperature, but at high temperatures behaves very similarly to raw natural rubber.

Analytical methods of this type lead, therefore, to a fairly accurate prediction of the nature of the dependence of deformation on time and temperature.

A second type of analytical method, which is purely mathematical, has

been developed by Kargin and Slonimsky[14] on the basis of Boltzmann's theory of elastic after-effects. A general equation is developed:

$$S(t, \epsilon) = E\epsilon(t) - \int_o^t f(t - \tau)\epsilon(\tau)dt \tag{3}$$

where S is stress, ϵ is strain, E is an elastic modulus, t the time of deformation, and τ an instantaneous value of t. In this integral equation, $f(t - \tau)$ is a nucleus which characterizes the mechanical properties of the material. As an example of the application of this method, consider the substitution of the special nucleus $f(t - \tau) = \frac{E}{T} e^{(-t-\tau)/T}$ in Equation 3.

$$S(t, \epsilon) = E\epsilon(t) - \int_o^t \frac{E}{T} e^{(-t-\tau)/T}\epsilon(\tau) \cdot dt$$

On differentiating both sides of this equation:

$$\frac{dS}{dt} = \frac{Ed\epsilon}{dt} - \frac{E}{T} e^{(-t-\tau)/T}\epsilon(\tau)$$

If the relaxation time T approaches infinity (case of a rigid elastic solid), $e^{(-t-\tau)/T} \rightarrow 1$, and thus:

$$\frac{dS}{dt} = \frac{Ed\epsilon}{dt} - \frac{E\epsilon}{T}$$

$$= \frac{Ed\epsilon}{dt} - \frac{s}{T}$$

i.e., Maxwell's equation is obtained as a particular solution. The function $f(t - \tau)$ may be represented approximately as a sum of exponential functions:

$$f(t - \tau) = \sum_{i=1}^{n} \frac{E_i}{T_i} e^{(-t-\tau)/T_i} \tag{4}$$

For the case of relaxation, Equations 3 and 4 give:

$$S = \sum_{i=1}^{n} E_i\epsilon_o e^{-t/T_i} \tag{5}$$

and for deformation at a constant rate of strain ($\dot{\epsilon}$ = constant):

$$S = \sum_{i=1}^{n} \eta_i\dot{\epsilon}_o(1 - e^{-t/T_i}) \tag{6}$$

η being a viscosity coefficient. Thus for times, t, small compared with the smallest relaxation time T_i, Equation (5) gives:

$$S = \sum_{i=1}^{n} E_i\epsilon_o \tag{7}$$

and the material obeys Hooke's law and has a Young's modulus:

$$E = \sum_{i=1}^{n} E_i$$

in Equation (6) for times t large compared with the largest relaxation time T, T:

$$S = \sum_{i=1}^{n} \eta_i \epsilon_o \tag{8}$$

that is, the material satisfies Newton's law and has a viscosity coefficient:

$$\eta = \sum_{i=1}^{n} \eta_i$$

Two interesting points emerge from this treatment. First, there is a general integral equation describing the deformation of real materials, in which the ideal cases of elastic solids and Newtonian fluids appear as special solutions and, secondly, $f(t - \tau)$ is a steadily decreasing function, which characterizes the fall with time of the influence of previous deformations, a phenomenon already recognized in rubberlike materials as memory or previous history.

The mathematical theory can be most simply represented graphically (Figure 1). For deformation at a constant rate, Hooke's law gives a beam

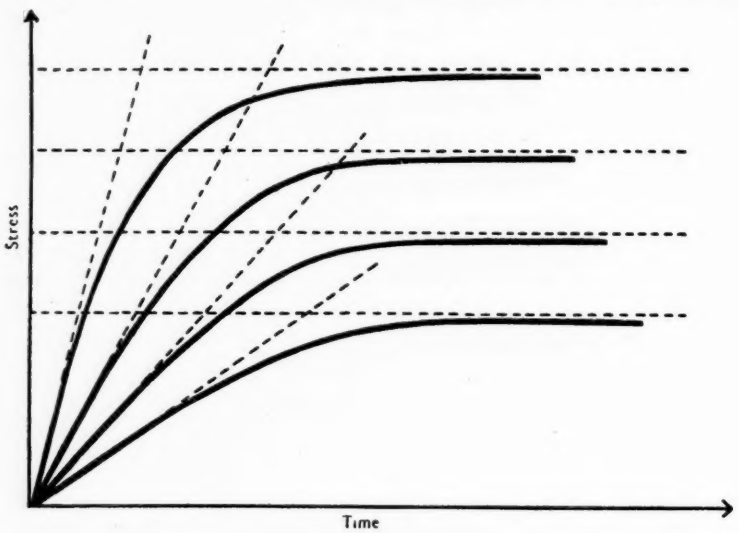

FIG. 1

of straight lines with slopes which depend on the rate of deformation, whereas Newton's law gives a system of straight lines parallel to the time axis. The stress-time relationship for elasto-viscous substances such as rubber is shown by the family of full curves tending to the corresponding asymptotes. A similar result has also been derived by the integrative method used by Scott-Blair and Coppen,[15] Broome and Bilmes[16] and others[17] in the study of deformation. In this case, relationships for the states intermediate between elastic solids and true fluids, have been deduced empirically. Thus in the case of:

an elastic solid	$n = S\sigma^{-1}t^{o}$
a true fluid	$\eta = S\sigma^{-1}t'$
real material	$\psi = S\sigma\ {}^{1}t^{k}\mathrm{o} < k \leqslant 1$

(9)

where n = rigidity modulus, S = applied stress, σ = strain, t = time, and η = coefficient of viscosity.

Thus, a general equation should describe the range of real materials, in terms of the dimensionless parameters ψ and k.

The values of these parameters are independent of stress and time of test, and the significance of ψ lies between elastic modulus and viscosity coefficient, and k is best described as "a measure of the extent to which time affects deformation."

Scott-Blair and Caffyn[18] have frequently suggested that these constants have more than an empirical significance, and the present authors feel that the foregoing discussion provides supporting evidence for this view, although it is difficult at the moment to interpret the exact relationship between the different theories. The factor common to all is the forecast of dependence of deformation on time, the Nutting-Scott-Blair relationship beingsome what limited in its application, due to omission of a temperature factor.

It is believed that the extension of this Equation (9) to the study of rubberlike materials has been undertaken for the first time in the present paper, with a measure of success adequately illustrated by experimental data.

In an early form of the equation, Nutting introduces a stress index β:

$$\sigma = \frac{S^{\beta} t^{k}}{\psi}$$

and β was quoted as having a high value for materials of a rubbery texture. Scott-Blair has found that, for materials containing rubber, $\beta = 1$, and the authors have preferred to assume $\beta \cong 1$ for this work. The explanation of the discrepancy in β values lies probably in the fact that the small strains (0.002) observed by Nutting occur in the region of truly elastic deformation.

In considering the experimental data discussed in the present study, it should be remembered that the three more usual modes of deformation have been employed, and no attempt has been made to design special apparatus, the machines are those normally in use in the rubber industry.

The significance of time effects.—The experimentally determined values of the characteristics which describe the behavior of real materials depend on the strain and rate of strain used in their measurement. Scott-Blair and Caffyn[18] have suggested that judgments of strain and of rate of strain in hand tests, are related by a principle of indeterminacy similar to that of Heisenberg, but with a much larger quantum constant, *i.e.*:

$$\Delta\sigma \cdot \Delta\dot{\sigma} \cong Q \qquad Q \gg h$$

a suggestion of obvious importance in the design of experiments.

The characteristics used to describe real materials depend on the extent of strain and the rate of strain used in their measurement. Let ϕ_1 be the extent to which a single constant defined by stress and strain alone describes the mechanical properties of a material. As in Figure 3, ϕ_1 is unity for a true solid, and decreases to zero for a true fluid. If ϕ_2 is the extent to which a single viscosity coefficient, determined only by stress and rate of strain, can describe the properties, ϕ_2 is unity for a true fluid and decreases to zero for a true solid.

Let ϕ be the total extent to which strain and rate of strain determine the mechanical characteristics of a material, then:

$$\phi = \phi_1 + \phi_2$$

If now k is identified with ϕ, the same values of k (or ϕ) can be expected for elastic solids and dilatant materials (low k), or fluids and thixotropic systems (high k), and this is in accordance with the anomalous k values observed by Scott-Blair. In particular, Figure 3 shows that materials at A (plasto-elastic) and at B (visco-elastic) could have the same k values, which corresponds to the confusion existing in the use of these terms

Rubber in compression.—The flow relationships of raw unvulcanized rubbers are determined in various types of plastometers for control purposes. Simple compression of a cylindrical rubber sample gives the complex type of curve shown in Figure 2.

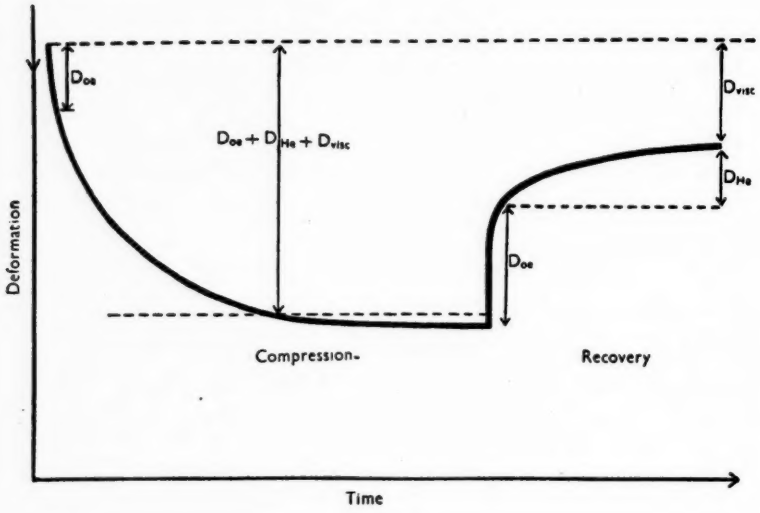

FIG. 2.

Over the first infinitesimal strains, the deformation is truly elastic. Highly elastic deformation and viscous flow proceed together, and the exponential form of the highly elastic orientation process, principally determines the curvature of the deformation relationship.

If sufficient time is allowed for the highly elastic deformation to develop fully, viscous flow can then proceed at an ever decreasing rate. On removal of the stress, immediate recovery of the truly elastic deformation occurs, followed by the slower recovery of D_{He}. Viscous flow is irreversible, and a permanent deformation due to this factor remains.

It is clear from the curve that the deformation relationships in compression are much more complex than in relaxation. For this reason the authors have preferred to study compression data to obtain data for practical purposes, while remembering the contribution of individual components in deformation. By this method the authors trace relationships between the classically divided strains and the complex integrations used in practice to judge the behavior of rubber.

In this case the Nutting-Scott Blair relationship has been found to hold:

$$\psi = S\sigma^{-1/k}$$

Rubber in extension.—The stress-strain properties of rubber are normally determined in extension, and the relationship is characteristically S-shaped. Anthony and Guth[19] have recently shown that this shape can be accounted for by separating the contributions to the total stress, due to internal energy changes and entropy changes.

For practical test purposes rubber is extended at a constant rate, and the characteristics of the stress strain curve depend on rate of deformation and temperature as before.

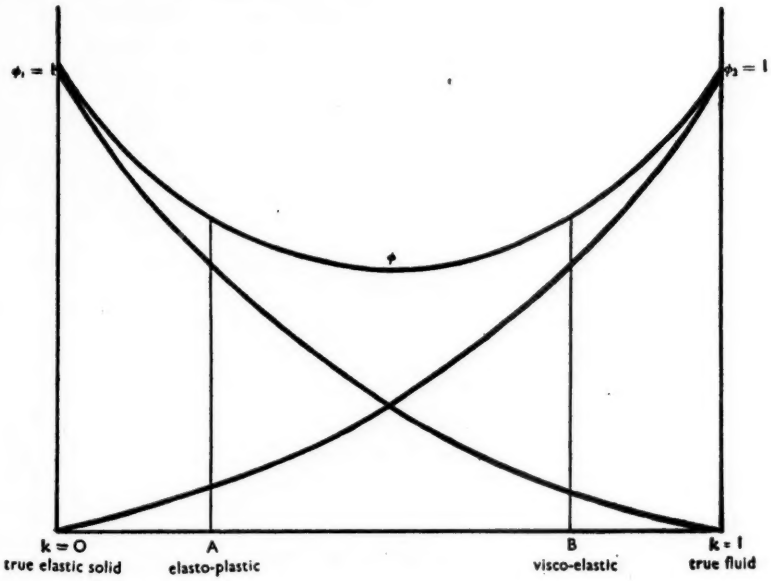

FIG. 3.—Uncertainty of judgment of plastic-elastic properties.

Empirically, in the following cases for:

$$\text{a true elastic solid } n = S\dot{\sigma}^{o}\sigma^{1} \text{ where } \dot{\sigma} = \frac{d\sigma}{dt} = \text{rate of deformation,}$$

$$\text{and a true fluid } \eta = S\dot{\sigma}^{1-}\sigma^{o}, \text{ and for}$$

$$\text{intermediate materials } \psi^{1} = s\dot{\sigma}^{-k'}\sigma^{k'-1} \tag{10}$$

where ψ' and k' may not correspond to the ψ and k of the original equation.

If $\dot{\sigma}$ be written as $\frac{\sigma}{t}$ (a relative velocity), this form reduces to the original Equation (9).

Rubber in shear.—Rubber in shear presents practical problems of first rate importance in the utilization of rubber for engineering purposes.

Flow can occur in vulcanized rubbers under constant load for long periods. This phenomenon is known as creep. Creep phenomena may be studied in shear or under compression, and the behavior in both cases is similarly explained. Initially, a small truly elastic strain is observed, followed by the slow development of highly elastic deformation, and later by viscous flow.

The accuracy of this picture is shown by the explanation of the processes occurring on removal of the load, which are first an initially rapid retraction due to instantaneous recovery of the truly elastic strain; secondly, slow relaxation of highly elastic deformation, which is assisted by heating, and thirdly, the remaining deformation is irreversible and is due to irreversible viscous flow, *i.e.*, permanent set.

Creep is a technical term, and is best regarded as a special case of the deformation shown in Figure 2, of special interest because it occurs in vulcanized rubbers. Due to the greater stability of the cross linkages in vulcanized rubber (sulfur linkages) compared with those in raw rubber (mechanical linkages), much higher stresses are necessary to cause chains to glide over one another in viscous flow. Internal stresses due to retractive tendencies increase as deformation proceeds, and small applied stresses are neutralized in a fairly short time and deformation ceases. If the applied stress is much greater than any internal stresses which can be built up, continuous deformation is possible.

A special case of the Equation (9) is used to describe creep phenomena.

The "creep" strain $= \sigma_t - \sigma_o$ where σ_t = total strain at time t, and σ_o = initial deflection. Thus

$$\sigma = \frac{\sigma_t - \sigma_o}{\sigma_o}$$

Hence

$$\psi = S_o \left[\frac{\sigma_t}{\sigma_o} - 1 \right]^{-1} \cdot t^k \tag{11}$$

EXPERIMENTAL

The ideal synthetic rubber would possess the processing characteristics of the natural product, but no such rubber has been found. It is obviously more important that the synthetic rubber should be more similar to the natural product after vulcanization than before, as use is more important than production technique. The rubber technologist has realized that each of these materials requires its own peculiar conditions for processing. He has automatically adapted his techniques and changed his processes to meet the exigencies demanded by each of the synthetic materials occupying a position on the plastic-elastic scale.

The conclusions reached in this work confirm the changes which it has been found necessary to make in the handling of the new synthetic rubbers.

The following representative rubbers have been chosen, natural rubber, GR-S (butadiene-styrene interpolymer), Neoprene-GN (chloroprene interpolymer), Novoplas-A (a thioplast type) and Butyl (butadieneisobutylene copolymer). The experimental work carried out falls into and is described in sections defined by the type of deformation under consideration.

Rubber in compression.—Our first aim was to fix the position of the raw materials on the plastic-elastic scale to assess the handling properties of these rubbers.

Raw rubbers.—With the Williams parallel-plate plastometer, readings of the compressed height were taken every five seconds during the three-minute compression cycle.

Williams and others obtained the values of the strain from the formula:

$$\sigma = \int_h^{h_t} \frac{dh}{h} = \log_e \frac{h_t}{h_o} \tag{12}$$

where h_t = compressed height at time t seconds and h_o = the original height. The limiting case of the formula above is:

$$\sigma = \frac{\Delta h}{h_o}, \quad \text{since} \quad \underset{h_t \to h_o}{L_t} \log_e \frac{h_t}{h_o} = \frac{\Delta h}{h_o}$$

where Δh = compression at time t seconds and h_o = the original height.

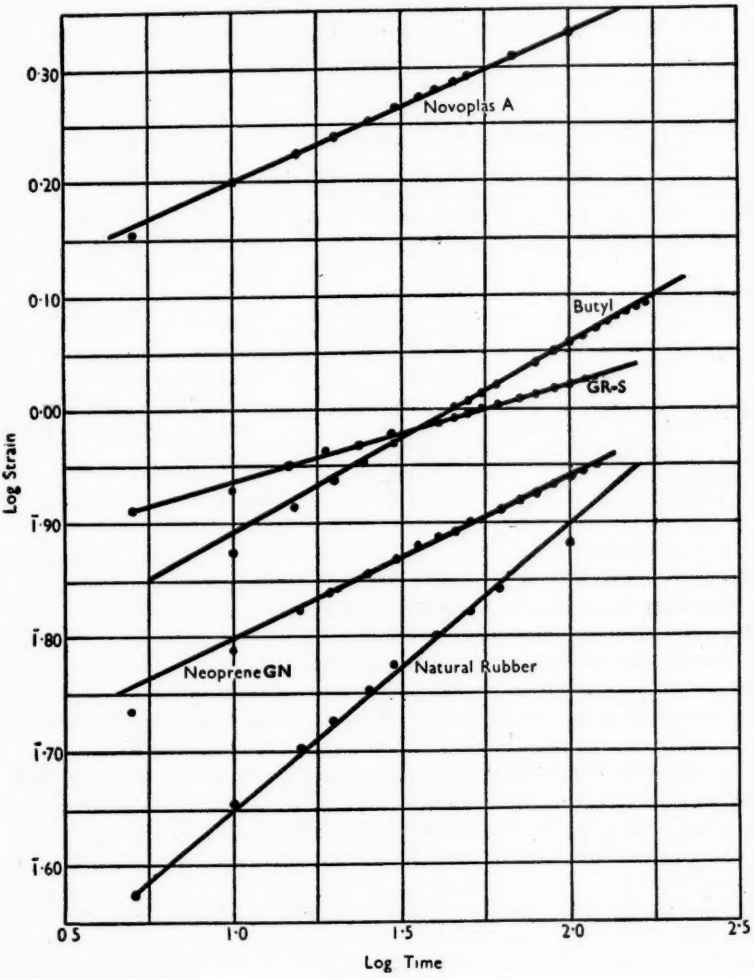

FIG. 4.

Williams used the above limit $\Delta h/h_o$, and obtained straight lines when he plotted log σ against log t. The limit $\Delta h/h_o$ can only hold for small strains, and for larger strains it is necessary to use the full equation, and this has been done in the present work.

Position of raw rubbers on plastic-elastic scale.—Samples of the five rubbers were put on a 12-inch laboratory mill and given the minimum amount of milling required to give a coherent mass. Cylinders were then prepared, and compression-time curves obtained in the Williams plastometer at 82.5° C.

Log σ was plotted against log t, and the straight lines obtained are shown in Figure 4.

It will be noted that, after the initial period, where there are accelerations present, good linear curves are obtained, and the use of the Nutting-Scott-Blair equation is therefore justified. The authors are aware that constant stress is specified for the application of this equation, but the results obtained indicate that this dependence on constant stress may not be so critical as hitherto believed. Constant stress is a condition which it is difficult to reproduce, and even such notable attempts as Scott-Blair's apparatus do not take into account the fact that, while the applied stress is constant, the internal stress induced in the specimen by the varying strain is changing.

The values k and log ψ obtained from the straight lines in Figure 4 are given in Table 1, and throughout the work the shear stress has been taken as

TABLE I

RAW MATERIALS

Material	k	log ψ	% Recovery after 2 min.
Natural rubber	0.247	6.2873	48
Butyl	0.166	5.8596	47
Neoprene-GN	0.140	6.0585	78
Novoplas-A	0.112	5.3865	24
GR-S	0.130	5.9135	75

$\frac{1}{3}$ of the compressive stress.

% Recovery $= H_R - H_c/H_c \times 100$, where H_R = height at 2 minutes after removing load and H_c = height at 3 minutes' compression.

Effect of milling.—The raw rubbers were milled for 5, 10, 20 and 30 minutes on a 12-inch laboratory rubber mill, with cold rolls, and cooling water turned full on. Compression-time curves were obtained as before, and straight lines, similar to those shown in Figure 4, obtained when log σ was plotted against log t.

The values of k and log ψ obtained from the graphs are given in Table 2.

Owing to the lack of tack of GR-S, difficulty was experienced in the preparation of cylinders. The figures given in Talbes 1 and 2, refer to a different sample of GR-S than the one used to obtain the data given in Tables 3, 4, 6 and 8.

Effect of temperature of test.—Cylinders cut from the unmilled rubbers were tested at 25°, 70°, 82.5° and 100° C. These tests were carried out a week after the results quoted in Table 1, and a comparison of the results at 82.5° is given in Table 3.

The results given in Table 4 show the effect of temperature of test on the k and log ψ values of the raw unmilled rubbers.

Vulcanized rubbers.—Having fixed the position of the raw rubbers on the plastic-elastic scale, a study of the flow properties of the vulcanized rubbers in the B.S. Gardness test[20] was made.

TABLE 2

EFFECT OF MILLING

Time of milling	Unmilled			5′			10′			20′			30′		
Material	k	$\log \psi$	% Recovery	k	$\log \psi$	% Recovery	k	$\log \psi$	% Recovery	k	$\log \psi$	% Recovery	k	$\log \psi$	% Recovery
Natural rubber	0.247	6.2873	48	0.166	5.8596	22	0.164	5.6119	17	0.156	5.5213	18	0.143	5.3547	23
Butyl	0.166	5.8596	27	0.167	5.8532	30	0.173	5.8764	28	0.166	5.8341	40	0.166	5.8341	41
Neoprene-GN	0.140	6.0585	78	0.151	5.8155	43	0.149	5.7425	31	0.151	5.6442	23	0.158	5.5400	22
Novoplas-A	0.122	5.3865	24	0.129	5.2127	28	0.160	5.2660	27	0.144	5.2601	30	0.146	5.2532	29
GR-S	0.130	5.9135	75	0.117	5.8152	59	0.124	5.7956	48	0.120	5.7743	52	0.111	5.7311	44

TABLE 3

RECOVERY OF RAW RUBBERS

Period of rest between milling and testing	1 day			8 days		
Material	k	$\log \psi$	% Recovery	k	$\log \psi$	% Recovery
Natural rubber	0.247	6.2873	48	0.310	6.6330	49
Butyl	0.166	5.8596	27	0.181	6.2150	24
Neoprene-GN	0.140	6.0585	78	0.134	6.2245	64
Novoplas-A	0.112	5.3865	24	0.123	5.8140	27
GR-S	0.079	5.9135	96	0.087	5.9720	81

TABLE 4

EFFECT OF TEMPERATURE OF TEST

Temperature test	25° C			70° C			82.5°			100° C		
Material	k	$\log \psi$	% Recovery	k	$\log \psi$	% Recovery	k	$\log \psi$	% Recovery	k	$\log \psi$	% Recovery
Natural rubber	0.307	7.2775	—	0.310	6.6539	58	0.310	6.6330	49	0.351	6.4545	43
Butyl	0.181	6.6775	—	0.195	6.1890	40	0.181	6.2150	24	0.152	6.0920	17
Neoprene-GN	0.304	8.3825	—	0.176	6.3805	93	0.134	6.2245	64	0.117	6.0895	39
Novoplas-A	—	—	—	0.131	5.8775	30	0.123	5.8140	27	0.108	5.7640	25
GR-S	0.172	6.6275	—	0.096	6.1500	104	0.087	5.9720	81	0.085	6.0457	105

The following compounds were used:

Smoked sheet rubber	100	—	—	—	—
Crepe rubber	—	—	—	5	—
Butyl	—	106.5	—	—	—
Neoprene-GN	—	—	100	—	—
Novoplas-A	—	—	—	95	—
GR-S	—	—	—	—	100
Stearic acid	3	3	—	1	2
Zinc oxide	5	—	1	10	5
Magnesium oxide	—	—	4	—	—
Cottonseed oil	—	—	5	—	—
Semireinforcing carbon black	—	—	—	25	—
Channel black	47.5	70	35	—	50
Nonox-S	—	—	2	0.5	—
Pine tar	—	—	—	—	3
Sulfur	3	0.5	—	0.1	3
Mercaptobenzothiazole	0.85	0.5	—	0.2	1
Diphenylguanidine	—	—	—	—	0.25
Tetramethylthiuram disulfide	—	1.0	—	—	—
Cure at 141° C (min.)	45	60*	30	80	60

* Cured at 153° C

The hardness of the vulcanizates wes determined by the above test, taking readings of the indentation every five seconds. In a further set of experiments, the normal 535-gram load was replaced by a 1-kilogram load.

The strain is obtained from the same equation as that used for the plastometer, namely:

$$\sigma = \int_o^t \frac{dh}{h} = \log_e \frac{h_t}{h_o}$$

where $h_t = h_o$ − B.S.I. reading and h_o = initial height.

The stress per unit area is not constant throughout these experiments, but diminishes as the indentation increases. Table 5 illustrates the range of

TABLE 5

VARIATION OF STRESS WITH INDENTATION

Load	Range of B.S. reading	Range of stress per unit area (dynes per sq. cm.) × 10^7.
565 g.	48– 57	1.93–1.71
	87–104	1.34–1.27
1030 g.	73– 87	2.67–2.45
	114–130	2.28–2.29

stresses produced by the different loads throughout our experiments.

Even with this discrepancy from the requirement of having constant stress throughout the experiments, a linear relationship exists between $\log \sigma$ and $\log t$. The straight lines obtained in the case of the 565 g. load at 25° C are typical, and are given in Figure 5.

The effect of increasing the temperature of test at both loads is shown by Table 6 where the values of k and $\log \psi$ obtained at 25°, 50°, 70°, and 100°C are given.

Scorching.—Scorching tests assess the safety of compounds during mixing and serve also as an indication of the fluidity and set-up of the compound at the high vulcanization temperatures used in the production of moulded articles.

Three natural rubber compounds, using different accelerators, were made. Cylinders cut from these compounds were heated at 100° C for appropriate times. The rate of development of set-up at these times was obtained by an

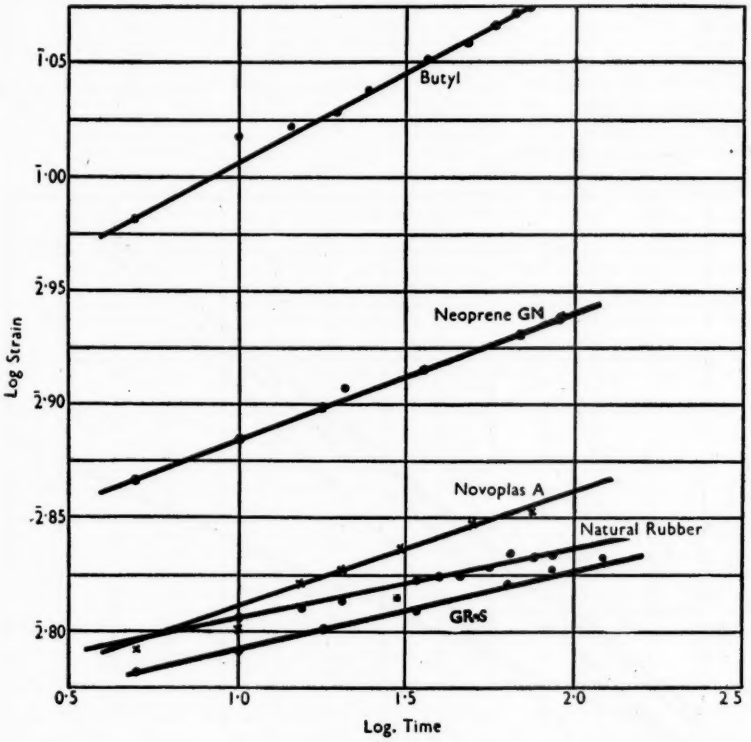

FIG. 5.

TABLE 6

VULCANIZED RUBBERS. EFFECT OF TEMPERATURE OF TEST

Temperature of test	25° C				50° C			
Load	565 g.		1030 g.		565 g.		1030 g.	
	k	$\log \psi$	k	$\log \psi$	k	$\log \psi$	k	$\log \psi$
Natural rubber	0.033	8.1229	0.033	7.9155	0.033	8.1068	0.022	7.9697
Butyl	0.081	7.8130	0.102	7.6969	0.057	7.6938	0.070	7.4573
Neoprene-GN	0.055	8.0350	0.065	7.8717	0.046	7.9910	0.046	7.7516
Novoplas-A	0.051	8.1850	0.063	8.1236	0.041	8.0573	0.048	7.9528
GR-S	0.035	8.1963	0.031	8.0068	0.034	8.1145	0.024	7.9929

Temperature of test	70° C				100° C			
Load	565 g.		1030 g.		565 g.		1030 g.	
	k	$\log \psi$	k	$\log \psi$	k	$\log \psi$	k	$\log \psi$
Natural rubber	0.022	8.0610	0.018	7.8836	0.019	8.0118	0.180	7.8544
Butyl	0.053	7.6359	0.070	7.4436	0.056	7.6295	0.052	7.2500
Neoprene-GN	0.046	7.9910	0.049	7.6672	0.044	7.8791	0.047	7.7053
Novoplas-A	0.084	7.9983	0.113	7.7311	0.278	8.2000	0.232	8.0009
GR-S	0.036	8.0405	0.022	7.9148	0.029	8.0352	0.031	7.9367

analysis of the deformation relationships measured in the Williams parallel-plate plastometer at 82.5° C.

The compounds used were:

Crepe rubber	100	100	100	100
Zinc oxide	10	10	10	10
Blanc fixe	75	75	75	75
Stearic acid	1	1	1	1
Sulfur	—	2.5	2.5	2.0
Dibenzothiazyl disulfide	—	0.5	—	—
Mercaptobenzothiazole	—	—	0.5	—
Tetramethylthiuram disulfide	—	—	—	0.375

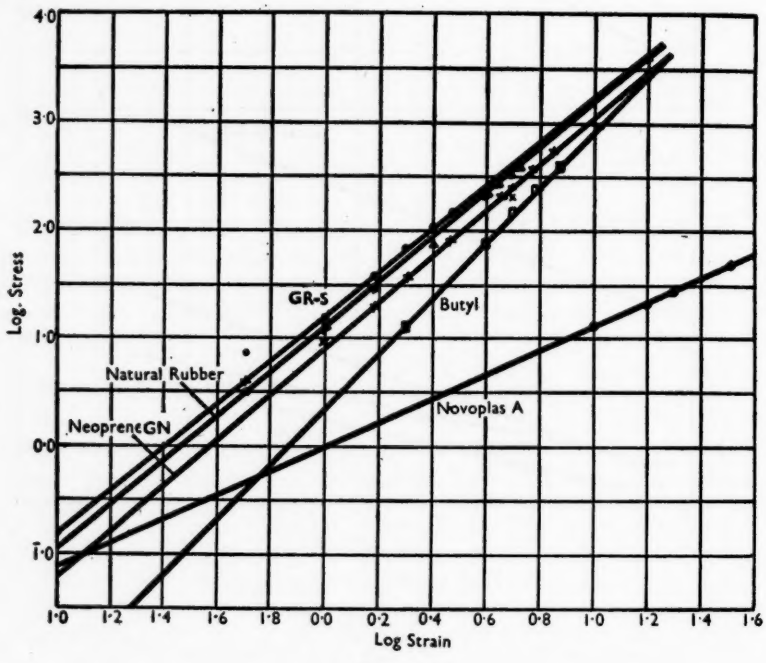

FIG. 6.

The values of k and $\log \psi$ obtained from the straight lines of the $\log \sigma / \log t$ graphs are given in Table 7.

TABLE 7

CHANGES IN k AND $\log \psi$ ACCOMPANYING SET-UP OF NATURAL RUBBER AT 100° C

Accelerator	Blank		MBTS		MBT		TMT	
Time of heating at 100° C	k	$\log \psi$	k	$\log \psi$	k	$\log \psi$	k	$\log \psi$
0 min.	0.156	6.0965	0.182	6.1940	0.136	6.0425	0.169	6.1305
30 min.	—	—	—	—	—	—	0.157	6.0805
45 min.	—	—	—	—	—	—	0.129	6.1525
60 min.	—	—	—	—	0.131	6.0085	0.124	6.2975
2 hours	—	—	0.140	6.0515	0.129	6.0315	—	—
3 hours	—	—	—	—	0.110	6.1555	—	—
4 hours	—	—	0.131	6.0480	0.086	6.3845	—	—
6 hours	—	—	0.073	6.0610	—	—	—	—

Vulcanized rubber in extension—stretching at constant rate.—The practical work carried out in this section has been confined to showing that Equation (10), derived in the theoretical part of this paper, describes the behavior of vulcanized rubbers in extension when stretched at a constant rate:

$$\psi' = S\dot{\sigma}^{-k'}\sigma^{k'-1} \tag{10}$$

Using ring test-pieces, the compounds described under compression hardness measurements, were tested on a Goodbrand tensile machine according to the British Standard Specification.[20] Three speeds of test, 40 cm., 20 cm. and 10 cm. per minute were investigated. On this instrument the stress was not constant, but the actual stress was read from the pendulum and the strain at that time obtained from the automatically recorded graph. The assumption that rubber does not change volume on stretching permitted the calculation of the real stress on obtaining the real cross section at each time interval.

The plot of $\log \sigma / \log S$ is remarkably linear in all cases and the straight lines obtained when the rate of stretching was 40 cm. per minute are given in Figure 6.

The values of k' and $\log \psi'$ obtained from the graphs are given in Table 8.

TABLE 8

EFFECT OF RATE OF STRETCHING ON k' AND LOG ψ'

Rate of stretching (cm. per min.)	40		20		10	
	k'	$\log \psi'$	k'	$\log \psi'$	k'	$\log \psi'$
Natural rubber	3.060	13.9957	3.135	13.7967	3.210	12.7078
Butyl	3.545	14.6947	3.725 (1)	14.5977 (1)	3.285 (1)	13.2078 (1)
			1.775 (2)	9.9217 (2)	1.715 (2)	9.7128 (2)
Neoprene-GN	3.130	13.9807	2.925	13.2146	2.775	12.5657
Novoplas-A	2.130	11.1757	1.915	11.5317	1.875	10.4478
GR-S	3.060	14.0807	2.975	14.5017	2.760	12.6578

Creep—Flow at constant load and/or constant deformation.—Vulcanized rubbers show a marked tendency to flow when they are subjected to high stresses for long times, and this flow process is generally referred to as creep, whether the rubber be subjected to constant load or constant deformation. The compounds listed below were tested in compression according to the constant deformation test.[21]

Natural rubber	100	—	—	—
Butyl	—	106.5	—	—
Neoprene-GN	—	—	100	—
GR-S	—	—	—	100
Stearic acid	3	3	1.0	2
Zinc oxide	5	—	5	5
Magnesium oxide	—	—	4	—
Tarine	1.5	—	—	3
Tricresyl phosphate	—	—	2.5	—
Channel black	50	50	36	50
Sulfur	3	0.5	—	3
Tetramethylthiuram disulfide	—	1.0	—	—
Mercaptobenzothiazole	0.85	0.5	—	1.0
Diphenylguanidine	—	—	—	0.25
Neozone-D	—	—	1.0	—
Vulcaflex-A	1	—	—	—
Cure at 141° C (min.)	45	60*	30	60

* Cured at 153° C.

The strain σ was calculated from Equation 12, and the log σ/log t straight lines are shown in Figure 7.

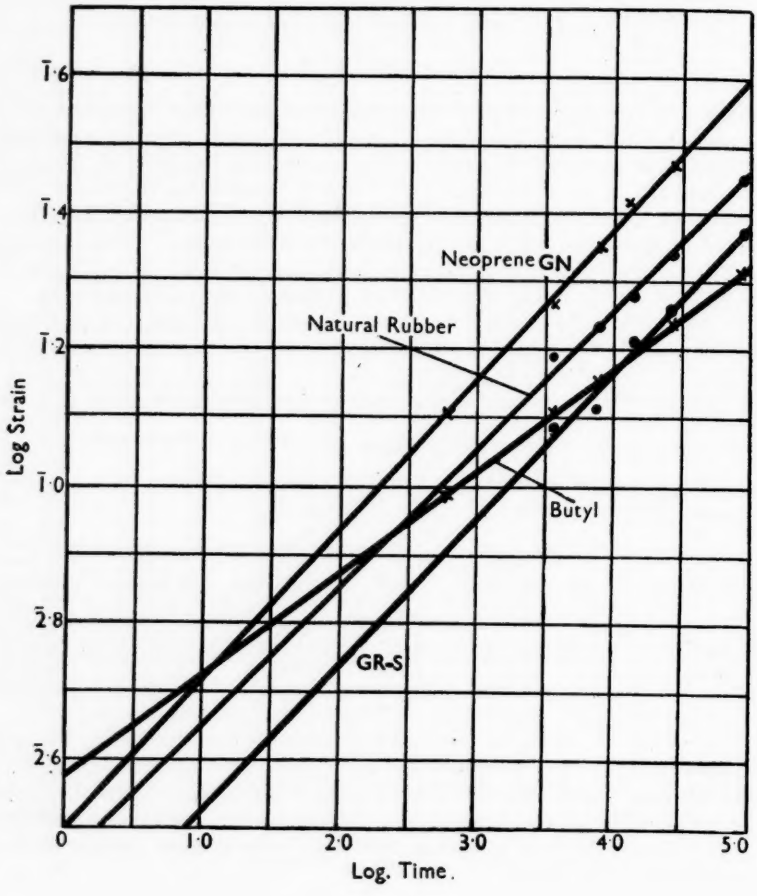

FIG. 7.

The values of k and log ψ obtained from Figure 7 are given in Table 9.

TABLE 9

VALUES OF k AND LOG ψ FOR RUBBERS UNDER CONSTANT DEFORMATION

Stress = 9.204×10^6 dynes per sq. cm.

	k	log ψ
Natural rubber	0.200	8.5091
Butyl	0.149	8.3921
Neoprene-GN	0.216	8.4591
GR-S	0.219	8.6691

Hahn and and Gazdik[22] investigated the effect of high shear-stresses acting over long periods of time (up to 900 days) at various temperatures. These

authors used the equations:

$$C\% = C_i t^n \tag{13}$$

or

$$\log C\% = \log C_i + n \log t \tag{14}$$

where $C\%$ = creep, C_i = constant, the intercept of the log-log curve at one day, n = constant, the slope of the log-log creep curve, t = time in days.

They obtained straight lines by plotting log $C\%$ against log t. They point out that two constants are obtained from their equation, but do not interpret the constants. Using our notation, k is the same as n and log ψ is the intercept on the log $C\%$ axis at log $t = o$. The values of k and log ψ calculated from Hahn and Gazdik's data are given in Table 10.

TABLE 10

VALUES OF k AND LOG ψ FOR RUBBERS IN SHEAR

Temperature of test	80° C		140° C		Creep properties of actual mountings as described by Hahn and Gazdik[22]
	k	log ψ	k	log ψ	
Natural rubber A	0.31	4.5595	0.40	4.5119	average creep
Natural rubber B	0.44	5.9173	0.52	5.5387	creep low but cannot carry load for a long period at 140° C
Natural rubber C	—	—	0.46	5.5387	low creep
Neoprene (type E)	0.31	4.5212	0.34	4.2607	best of 10 Neoprenes—four of which failed within 40 days at 140° C
Butadiene copolymer	0.21	3.7374	—	—	high creep—short life at 140° C
Copolymer	0.24	4.2843	0.35	4.7430	lowest creep

DISCUSSION

Before discussing the relative positions of different rubberlike materials on the plastic-elastic scale of rheological materials, it is essential that a clear picture of the position of the rubberlike state on this scale be obtained.

The three quantities ψ, k, and β define the characteristics of a rheological material, as k and β define the class of rheological materials and ψ defines the intensity of its properties in that class.

A two dimensional diagram, known as the "Nutting square" [23] has been designed to represent the various rheological classes. The Nutting square is reproduced in Figure 8.

Materials having $\beta = 1$ lie along the Scott-Blair-Coppen axis. A rough check on the validity of the assumption that $\beta = 1$ for the rubberlike state is obtained from Table 11, where the variation of log ψ with varying stress throughout a single test on natural rubber is given for two instruments.

TABLE 11

DEPENDANCE OF LOG ψ ON STRESS

Instrument	Range of stress (dynes per sq. cm.)	Range of log ψ
Williams Plastometer	5.185×10^5 to 3.9080×10^5	6.2873–6.2277
B.S.I. hardness gauge	1.93×10^7 to 1.71×10^7	8.0459–7.9851

Although log ψ is not constant and depends to some extent on the stress, the discrepancy is not great and the assumption that $\beta = 1$ for both the raw and vulcanized rubber can thus be justified at this stage in the work.

Thus within small deviations of β, the rubberlike state lies along the Scott-Blair-Coppen axis.

Rheological terminology in the rubber industry.—The rubber technologist already uses rheological terms such as nerve toughness, and logginess. Interpreting these properties in relation to k and $\log \psi$ nerve would be related to a low value of k, associated normally with high $\log \psi$. Toughness implies high $\log \psi$, and normally would be associated with low k. Logginess is related to high values of k along with low $\log \psi$.

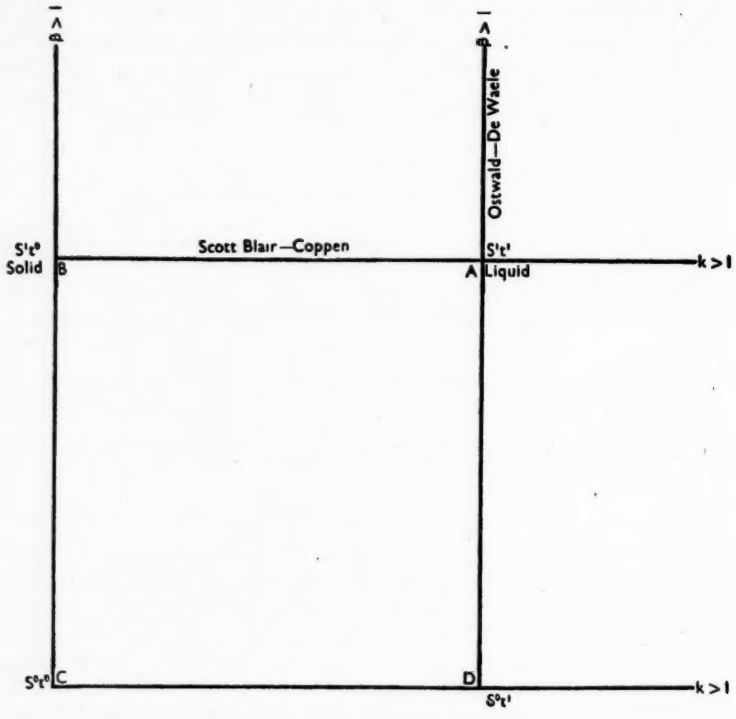

FIG. 8.—The Nutting square.

For the rubberlike state, the present authors are of the opinion that ψ should be considered as stiffness and would thus be defined as the reciprocal of the strain produced by unit stress in unit time, since

$$\log \psi = \log S - \log \sigma_t + k \log t$$

$$\text{then at } S = 1, \text{ and } t = 1, \log \psi = \frac{1}{\log \sigma_1},$$

It will be observed that percentage figures are quoted, but no attempt is made at analysis. These figures imply a division of strains into recoverable and irrecoverable components, and thus do not show any correlation with $\log \psi$ and k.

Position of raw rubbers on plastic-elastic scale.—Figure 9 has been constructed to show the relative positions of the five raw rubbers on the plastic-elastic scale. Natural rubber has the highest value of k and also the highest stiffness. This significant fact indicates clearly why natural rubber is easier to process

than any of the synthetics. Natural rubber's first attribute therefore lies in its position on the scale, along with its high degree of stiffness.

The four synthetic rubbers lie in the following order of decreasing values of k: Butyl, Neoprene-GN, Novoplas-A and GR-S, and processing would be expected to become more difficult as k is decreased for a given value of $\log \psi$. Practical experience agrees with this view. The anomalous position of Novoplas-A will be discussed later. From the above positioning it is easy to understand why small mill loadings of GR-S must be used, as a high value of $\log \psi$ implies low workability.

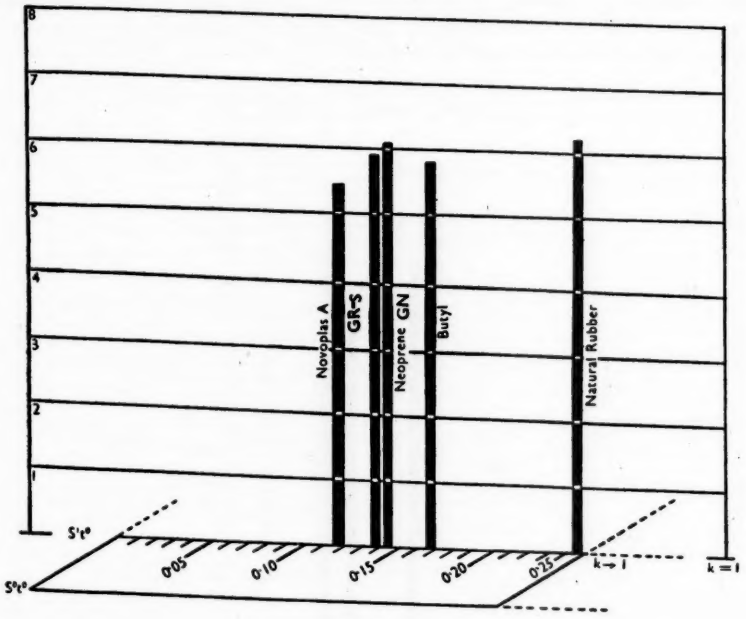

FIG. 9.

Effect of milling the raw rubbers.—Figure 10 has been constructed from the data in Table 2, showing the relative positions of the raw rubbers after 30 minutes' milling.

In all cases milling decreases the stiffness, $\log \psi$, that is, the rubber, shows a lower degree of resistance to deformation, or in the terminology of the rubber industry the rubber becomes more plastic.

After milling, all the raw rubbers occupy a narrower range on the plastic-elastic scale, and it is significant that even after 30 minutes' milling none of the synthetic rubbers has been moved to occupy the position of raw unmilled natural rubber. Thus it would appear to be impossible to make any of the above synthetic rubbers have either the ease of processing or stiffness of raw unmilled natural rubber by milling alone.

In the case of natural rubber k falls rapidly, during the first five minutes' milling and then falls more slowly. This agrees with the theory of oxygen vulcanization occurring during milling.[24] It is reasonable to suppose that this vulcanization would be most rapid in the early stages of milling when fresh surfaces are exposed for the first time.

Butyl rubber is left relatively unaffected even after 30 minutes' milling, and this maintenance of k and $\log \psi$ agrees with experience, and would be expected on the theoretical grounds, since Butyl rubber has a low degree of unsaturation. With Neoprene-GN, k increases, due to the breaking of cross links, thus permitting Neoprene-GN to exhibit a higher degree of flow.

GR-S is thought to be highly cross-linked, even in the raw material, agreeing with the low value of k, and the slight initial decrease in k may be due to oxygen vulcanization as with natural rubber, followed by the actual breaking of cross-links as k increases again slightly.

Recovery of raw rubbers.—From Table 3 it is seen that with all the rubbers, except Neoprene-GN, k increases. This is most probably due to internal stresses acting over a relatively long time. The recovery of the raw rubbers,

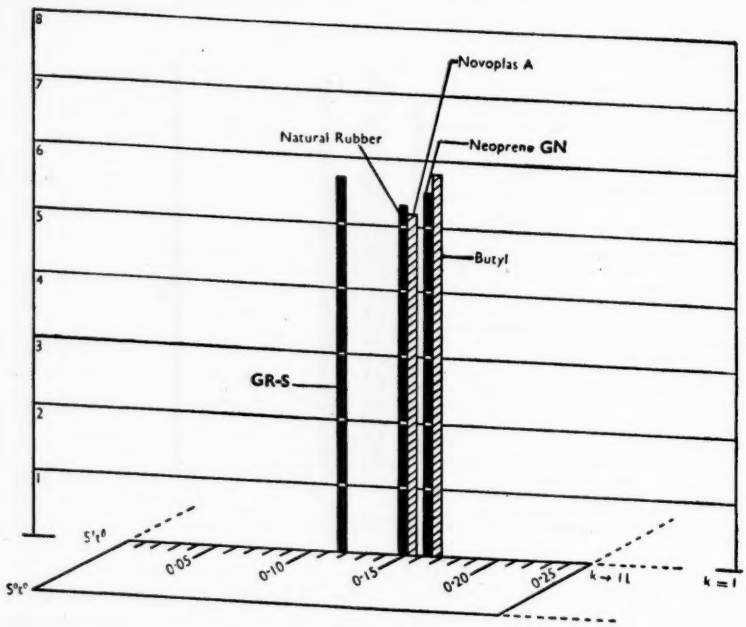

FIG. 10.

i.e., increased plasticity index, is evidenced in all cases by the increased value of stiffness.

Effect of temperature of test.—The fact that k decreases with increasing temperature with all the synthetic rubbers confirms the view that these materials develop their true rubberlike elasticity at higher temperatures than that characteristic of natural rubber. This being so, the orientation time for these products should be greater than the orientation time of natural rubber over the temperature range 70° to 100° C.

The exact relationships between $\log \psi$, k, and temperature are complicated by the presence of transition points, which would appear to be different for each material. Equation (9) does not take account of the effect of temperature and this must be regarded as a restriction in its application to rubberlike materials.

Position of valcanized rubbers on plastic-elastic scale.—From a study of the results given in Table 6, it is possible to construct Figure 11 showing the relative positions of the vulcanized rubbers on the plastic-elastic scale. The results obtained at 25° C with the 565-gram load have been used in Figure 11.

The most striking feature in Figure 11 is the new position of natural rubber. Vulcanization has moved natural rubber to the end of the scale and whereas, before vulcanization, natural rubber had the largest value of k, it now has the smallest. This is the second and probably most important attribute of natural rubber. It must be appreciated that the effect of compounding ingredients is also to decrease k and increase $\log \psi$, but at this stage the

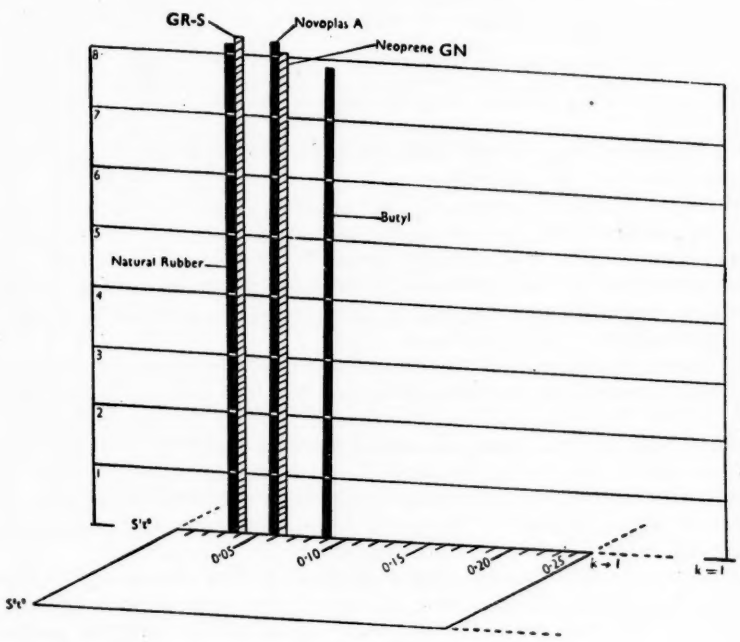

FIG. 11.

authors have not differentiated between the contributions from compounding and from vulcanization.

After vulcanization, GR-S occupies the same position as natural rubber, and has the same degree of stiffness, confirming the selection of GR-S as the most suitable synthetic product for replacing natural rubber. It should be noted, however, that the change in k produced by vulcanization is less in the case of GR-S than for natural rubber.

Neoprene-GN does not develop the same degree of cure as natural rubber, but is intermediate between natural rubber and Butyl, which has the lowest degree of cure. The results indicate that it is unfortunate that the degree of unsaturation in Butyl is so low.

The changes produced by compounding and vulcanization can be summarized by using an arbitrary term index of reënforcement, where reënforce-

ment is interpreted as any change in structure enhancing elastic properties:

$$\text{index of reënforcement} = I_R = \frac{k_o}{k_1} \tag{16}$$

where $k_o = k$ for raw unmilled rubber and $k_1 = k$ for vulcanized rubber. Then

$$I_R = I_c + I_v$$

where I_c = index of compounding and I_v = index of vulcanization.

The following values of I_R are obtained from the results:

	Index of reënforcement
Natural rubber	7.5
Butyl	2.05
Neoprene-GN	2.54
Novoplas-A	2.2
GR-S	2.25

It is significant that all the synthetic rubbers have a much lower index of reënforcement than natural rubber.

Effect of increasing the stress.—When rubbers are deformed, internal stresses oppose the applied stress, and when the applied stress is below a critical value, flow will diminish and finally cease. From Table 6 it is seen that the critical applied stress has not been exceeded in the case of natural rubber and GR-S, is about to be exceeded in the case of Neoprene-GN, and has been exceeded in the case of Butyl and Novoplas-A.

Effect of temperature of test.—At a fixed stress, raising the temperature moves the material into the region where it exhibits its true rubberlike elasticity. When the temperature is increased beyond the upper limit of the rubberlike temperature range, the position of the material is moved towards the fluid state. Increasing the applied stress displaces the positions to an extent which depend on the critical value of the applied stress, and a new orientation time is defined by the temperature range over which the displaced rubbers will exhibit their rubberlike elasticity.

Anomalous results obtained with Novoplas-A.—The anomalous position of Novoplas-A can be accounted for in the terms used previously to explain that k may have the same value for materials having widely different properties. Novoplas-A would be normally classified as a thermoplastic, and its thermoplastic nature dominates its behavior. Novoplas-A really lies well outside the region of the rubberlike state, towards the fluid end of the plastic-elastic scale.

TABLE 12

Accelerator	TMT	MBT	MBTS
t	34.5 min.	1 hr. 58.5 min.	4 hr. 52 min.
k	0.150	0.129	0.112
$\log \psi$	6.5716	6.5066	6.5306

The low values of k which have been found can, therefore, be explained as in the earlier discussion on the significance of k.

Scorching.—From Table 7, k decreases progressively as the scorching time is increased, whereas the stiffness ($\log \psi$) decreases, due to peptization by the accelerator, and then increases as scorching is promoted.

The change in k and $\log \psi$ with time of scorching at 100° C is shown in Figure 12.

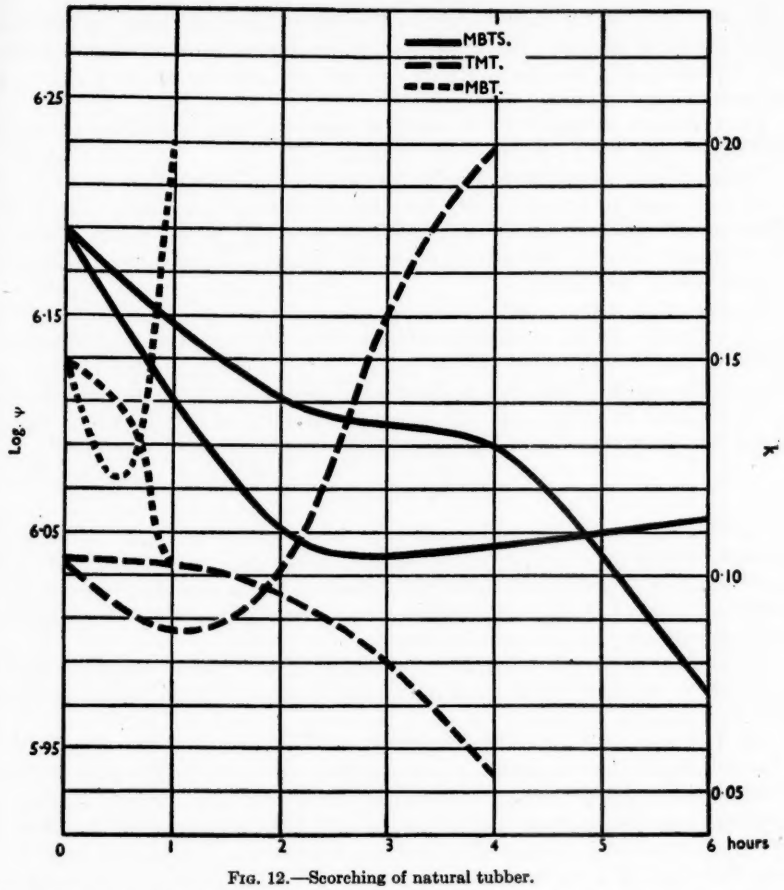

FIG. 12.—Scorching of natural tubber.

N.B.—The k Scales for MBTS, TMT have been altered to represent the six curves on one diagram.

It is interesting to note that the point of intersection of k and $\log \psi$ occurs at the scorching time which would be determined by the rubber technologists. The values of $\log \psi$ and k at the scorching times, are given below in Table 12.

Rubber in extension.—Equation (10) is intended to be complementary to the Nutting-Scott-Blair Equation (9). It should be of general application, but in the special case considered, $\dot{\sigma}$ is constant. This control of $\dot{\sigma}$ would appear to be no more artificial than the use of constant stress. The values of $\log \psi'$ and k' for the five rubbers studies are given in Table 8, and it is seen that the true rubbers appear to be characterized by a $\log \psi'$ value in the region of 13–14, and k' about 3. Novoplas-A, and Butyl in the early stages of extension are much further removed from the true rubbers, by this analysis, than by the previous one. Butyl rubber is characterized at the slower speeds by the appearance of a $\log \sigma / \log S$ relationship consisting of two straight lines and the appropriate values of $\log \psi'$ and k' have been given as (1) and (2) in Table 8. This agrees with the well known pecularities of the stress-strain curve for this material.

On the basis of the uncertainty of the dependance of stress on strain and rate of strain, Equation (10) would appear to define more absolute constants than Equation (9), but the authors are not yet able to assess the true significance of $\log \psi'$ and k'.

The influence of speed of test on $\log \psi'$ and k' is seen to be least for natural rubber, and greatest in the case of Neoprene-GN.

Creep.—From Hahn and Gazdik's data given in Table 9, it is possible to assess the values of k and $\log \psi$ associated with good creep properties. High stresses operating for long times produce viscous flow; hence the higher values of k obtained in creep data, compared to the values of k for vulcanized rubbers given earlier in this paper.

It appears that the conditions for good creep are low values of k and high values of $\log \psi$. With synthetic rubbers, therefore, the creep properties are limited in the first instance by the values of these constants for the raw materials. The second limitation is the value of the index of reënforcement which can be induced by fillers and vulcanization, and the extent to which stiffness ($\log \psi$) can be increased for a given index of reënforcement.

SUMMARY

(1) Young's modulus and coefficient of viscosity are not sufficient to characterize the deformation of rubberlike materials. New constants are required to describe rubberlike behavior, which shows a complex dependence on strain and rate of strain. Analytical and integrative methods are shown to lead independently to this conclusion.

(2) The behavior of rubberlike materials can be described equally well by empirical or mathematical equations, which contain ideal cases as special solutions.

(3) The equation derived by Nutting and by Scott-Blair for measurement of the firmness of soft materials has been shown to apply to the case of rubber in compression, ψ has been interpreted as stiffness, k as a measure of the time dependence of deformation, and a new Index I has been introduced to describe the changes in state, produced by technical processes. A special case of the Scott-Blair equation for extension at a constant rate, has been suggested:

$$\psi' = S\dot{\sigma}^{-k'}\sigma^{k'-1}$$

where ψ' and k' are constants.

(4) The parameters (ψ, k) of the rubberlike state for natural rubber, Neoprene-GN, Butyl rubber, GR-S and Novoplas-A in the raw state, and the positional changes induced in these materials by mastication, vulcanization and reënforcement have been determined. Technical data such as creep have been interpreted on this basis.

(5) A method of representing the properties of rubberlike materials, by 3-dimensional diagrams involving ψ, k and β has been introduced.

(6) The uncertainty in measurements of the constants of real materials such as rubber, has been considered and an explanation offered for anomalous values of k.

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REFERENCES

[1] Bresler and Frenkel, *Acta Physicochimica U.R.S.S.* **11**, 485 (1939); Bunn, *Proc. Royal. Soc.* **180A**, 40 (1942).
[2] Meyer, *Angew. Chem.* **50**, 328(1937).
[3] Slonimskiy, *Acta Physicochimica U.R.S.S.* **12**, 99 (1940).
[4] Buist, *Nature* **149**, 702 (1942).
[5] Aleksandrov and Lazurkin, *Acta Physicochimica U.R.S.S.* **12**, 647, 669 (1940).
[6] Kuhn, *Kolloid-Z.* **76**, 253 (1936); *Z. physik. Chem.* **42B**, 1 (1939); Meyer, Valko and von Susich, *Kolloid-Z.* **54**, 208 (1932).
[7] Kobeko, Kuvshinskiy and Gurevich, *Tech. Physics U.R.S.S.* **4**, 622 (1937).
[8] Gurevich and Kobeko, *Acta Physicochimica U.R.S.S.* **12**, 681 (1940).
[9] Eley, *Trans. Faraday Soc.* **38**, 303 (1942).
[10] Kauzmann and Eyring, *J. Am. Chem. Soc.* **62**, 3113 (1940); Rooseveare, Powell and Eyring, *J. Applied Physics* **12**, 669 (1941); Smallwood, *J. Applied Physics* **8**, 505 (1936).
[11] Aleksandrov and Lazurkin, *Acta Physicochimica U.R.S.S.* **12**, 647 (1940).
[12] Tuckett, *Trans. Faraay Soc.* **38**, 310 (1942).
[13] Ueberreiter, *Z. physik. Chem.* **45B**, 361 (1940).
[14] Kargin and Slonimskiy, *Acta Physicochimica U.R.S.S.* **12**, 931 (1940).
[15] Scott-Blair and Coppen, *J. Soc. Chem. Ind.* **60**, 190 (1941).
[16] Broome and Bilmes, *J. Soc. Chem. Ind.* **60**, 194 (1941).
[17] Couzens and Wearmouth, *J. Soc. Chem. Ind.* **61**, 69 (1942); Nutting, *J. Am. Chem. Soc. Testing Materials.* **21**, 1162 (1921).
[18] Scott-Blair and Caffyn, *J. Sci. Inst.* **19**, 88 (1942).
[19] Anthony and Guth, *J. Phys. Chem.* **46**, 826 (1942); *Ind. Eng. Chem.* **34**, 1349 (1942).
[20] British Standards Specification, **1940**, p. 903.
[21] Am. Soc. Testing Materials, *Standards on Rubber Products* **1937**, D, 395–37T.
[22] Hahn and Gazdik, *India Rubber World*, **103**, 51 (1941).
[23] Nutting, *J. Am. Soc. Testing Materials* **21**, 1162 (1921).
[24] Naunton and Morgan, *Proc. Rubber Tech. Conf. London* **1938**, p. 599.

STATISTICAL THERMODYNAMICS OF RUBBER. III*

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The kinetic theories of rubber elasticity which have been developed within recent years[1] have grown out of one fundamental idea, namely that the elastic forces involved are due to the thermal motions of the molecules rather than to deformations of valence bonds and angles. In deriving theoretical equations of state for rubber, the usual procedure has been to connect entropy concepts with the probability functions for molecular shapes, assuming that molecules can have different shapes as a result of rotation about some of the valence bonds. Although the various authors[1] started with substantially the same idea, their theories differed as to the way in which entropy changes were calculated. Recently, however, Treloar[2] has shown that by eliminating certain approximations from Kuhn's treatment[3], then Kuhn's theory gives precisely the same result as does the theory of the present author[4].

A basic postulate of the author's theory and of Kuhn's theory as amended by Treloar is that, when a piece of rubber is deformed, the components of the lengths of the molecules change in the same ratio as the corresponding dimensions of the rubber. To illustrate this specifically, let us consider a one-dimensional problem. If x is the component of the length of a molecule in the direction under consideration, then for a piece of unstrained rubber the probability of finding a molecule with a value of x in the range x to $x+dx$ will be given by:

$$p(x)dx = (\beta/\pi^{\frac{1}{2}}) \exp(-\beta^2x^2)dx \tag{1}$$

where β is a parameter which depends on the nature of the molecular chains. According to the above-mentioned postulate, when the rubber is stretched by a factor α, then the distribution function becomes:

$$p'(x)dx = (\beta/\pi^{\frac{1}{2}}\alpha) \exp(-\beta^2x^2/\alpha^2)dx. \tag{2}$$

Although Equation (2) is highly plausible and provides a convenient start for a theory of elasticity, it would be well to look into the reasons underlying it. One of the purposes of the present paper is to derive Equation (2) from more fundamental considerations. This will be accomplished by showing that (2) is the most probable distribution compatible with the strained condition of the rubber, it being assumed that (1) represents the distribution for the unstrained material.

A rubber network presumably consists of molecules linked together at various places by means of vulcanization bridges. Starting at one end of a piece of bulk rubber, one should be able to reach the other end by following a more or less random path of molecules through the network (Figure 1). Going from one end to the other by a random path involves a large number of molecules, and the path will include numerous retrogressions from, as well as advancements toward, the ultimate goal. It should be recognized that a few

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conceivable paths might involve a relatively small number of molecules if the paths happen to be fairly straight. Other paths on the other hand can involve an unduly large number of molecules. We shall here consider a typical random path involving, let us say, n molecules.

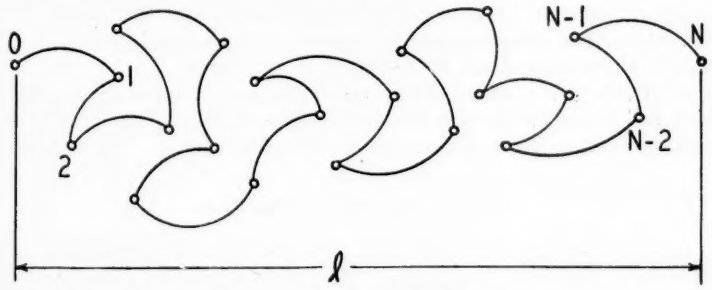

FIG. 1.—Random molecular path involving n molecules passing through network of rubber of length l. Small circles denote vulcanization bridges, each of which probably links together four "molecules". (To avoid confusion no side links are shown in the figure.)

If l equals the overall length of the rubber, then:

$$l = x_1 + x_2 + x_3 + \cdots x_n \tag{3}$$

where the x's denote the components of the lengths of the molecules in the direction considered. It should be noted that the x's can have positive or negative values, and that l is measured by their algebraic sum and not by the sum of their absolute values. Squaring (3) there is obtained:

$$l^2 = x_1^2 + x_2^2 + x_3^2 + \cdots x_n^2 + 2(x_1x_2 + x_2x_3 + \cdots x_{n-1}x_n) + 2(x_1x_3 + x_2x_4 + \cdots x_{n-2}x_n) + \cdots. \tag{4}$$

Since n is large, we can simplify (4) by introducing averages, thus obtaining:

$$l^2 = n\langle x^2\rangle_{Av} + 2(n-1)\langle x_ix_{i+1}\rangle_{Av} + 2(n-2)\langle x_ix_{i+2}\rangle_{Av} + \cdots. \tag{5}$$

But because n is large and the path is random, all of the averages appearing in (5) except $\langle x^2\rangle_{Av}$ approach zero, since the x's are divided almost equally between positive and negative values. Making use of this fact it is seen that:

$$l^2 = n\langle x^2\rangle_{Av}. \tag{6}$$

Equation (6) is not exact, but is an excellent approximation for the purpose in mind. As a matter of fact, Equation (6) gives exactly the mean square length of a large number of chains of n members, the average square lengths of the members being $\langle x^2\rangle_{Av}$, providing the chains are not subject to any boundary constraints. Since, for the problem at hand, the chains must begin and end in certain planes and cannot have any portions outside the boundaries of the bulk rubber, some degree of randomness is lost, thereby rendering (6) an approximation.

From Equation (6) we conclude that the overall length of a piece of rubber is proportional to the root mean square length of the molecules, referring of course to components in the specified direction. Accordingly if a piece of rubber is stretched from a length l to αl, then the root mean square length of

the molecules must be increased by a factor α. This statement is considerably more general than saying that each molecule has its length component changed by a factor α, for there are obviously many other ways of changing the root mean square length by a given factor.

There will now be derived the most probable distribution of molecular lengths consistent with a given macroscopic length for the piece of rubber. For convenience the one-dimensional problem will be considered first, and the extension to three dimensions made later.

Let us divide the x space of the molecules into a number of cells of size Δx_i, each cell being located in the neighborhood of x_i. Let the probability that a molecule have an x value in the range of Δx_i be p_i. Then from (1) we have:

$$p_i = (\beta/\pi^{\frac{1}{2}}) \exp(-\beta^2 x_i^2)\Delta x_i. \tag{7}$$

Let N_i equal the number of molecules with x values in the range Δx_i, and N equal the total number of molecules. Then the number of permutations associated with the statistical state specified by N_0, N_1, N_2, $\cdots$, etc. will be given by:

$$W = \frac{N!}{N_0!N_1!N_2!\cdots} p_0^{N_0} p_1^{N_1} p_2^{N_2} \cdots. \tag{8}$$

Two conditions of constraint can be applied to Equation (8), namely:

$$N = \sum_i N_i \tag{9}$$

and

$$l^2 = C \sum_i N_i x_i^2. \tag{10}$$

Condition (9) simply requires the correct sum for the total number of molecules, and condition (10), in which C is a constant, is equivalent to (6).

The statistical problem can now be carried out in the usual way[5]. To find the most probable distribution we make use of Stirling's approximation and note that:

$$\delta \ln W = \sum_i (-\ln N_i + \ln p_i)\delta N_i = 0,$$

$$\delta N = \sum_i \delta N_i = 0 \tag{11}$$

and

$$\delta l^2 = C \sum_i x_i^2 \delta N_i = 0.$$

Introducing Lagrangian multipliers in the conventional manner and solving for N_i there is obtained:

$$N_i = p_i \exp(\lambda + \mu x_i^2) \tag{12}$$

where the multiplier μ has absorbed the constant C. Putting in the value for p_i it is seen that:

$$N_i = (\beta/\pi^{\frac{1}{2}}) \exp\{\lambda - (\beta^2 - \mu)x_i^2\}\Delta x_i \tag{13}$$

or in a differential form:

$$dN = (\beta/\pi^{\frac{1}{2}}) \exp\{\lambda - (\beta^2 - \mu)x^2\}dx. \tag{14}$$

From (14) it follows that:

$$N = \frac{\beta e^{\lambda}}{\pi^{\frac{1}{2}}} \int_{-\infty}^{\infty} \exp\{-(\beta^2 - \mu)x^2\}dx = \frac{\beta e^{\lambda}}{(\beta^2 - \mu)^{\frac{1}{2}}}. \quad (15)$$

Eliminating e^{λ} from (14) and (15) we see that:

$$dN = \frac{N(\beta^2 - \mu)^{\frac{1}{2}}}{\pi^{\frac{1}{2}}} \exp\{-(\beta^2 - \mu)x^2\}dx. \quad (16)$$

But from (10) and (16) it follows that:

$$l^2 = \frac{CN(\beta^2 - \mu)^{\frac{1}{2}}}{\pi^{\frac{1}{2}}} \times \int_{-\infty}^{\infty} x^2 \exp\{-(\beta^2 - \mu)x^2\}dx = \frac{CN}{2(\beta^2 - \mu)}. \quad (17)$$

It is clear from (16) that the piece of rubber must be in its natural unstrained state when $\mu = 0$, under which condition $l = l_0$. Hence from (17):

$$l_0^2 = CN/2\beta^2 \quad (18)$$

from which it follows that:

$$\alpha^2 = (l/l_0)^2 = \beta^2/(\beta^2 - \mu). \quad (19)$$

Combining (19) with (16) there is obtained the equivalent of (2), namely:

$$dN = (N\beta/\pi^{\frac{1}{2}}\alpha) \exp(-\beta^2x^2/\alpha^2)dx. \quad (20)$$

The foregoing treatment shows that (2) or (20) must be the most probable distribution compatible with an increase in root mean square length by a factor α. Although (2) was a very plausible postulate, the present treatment strengthens it by showing what ideas are implicit in it. For one thing it is not necessary to suppose that each molecule is extended in the same way as the mass of rubber. Thus the postulatory basis of the theory of rubber elasticity has been pushed back at least one step toward more fundamental concepts, such as are illustrated in Figure 1 and expressed by Equations (3) to (6).

It is important that one deal with the root mean square length rather than with the average of the absolute values of the molecular lengths. If condition (10) were replaced by:

$$l = C \sum_i |x_i| N_i \quad (21)$$

then Equation (20) would not be obtained. Instead one would arrive at a less neat distribution function, which would ultimately lead to an unwieldy equation of state for rubber. Conditions of type (21) would also make the three-dimensional problem intractable with respect to change of coordinates, because the total length of a molecule cannot be taken as the sum of the three components, whereas the square of the total length is equal to the sum of the squares of the components. It should not be supposed, however, that (10) is more correct than (21) simply because it is easier to handle, for the theoretical considerations outlined earlier show that (10) is to be expected.

THE EQUATION OF STATE FOR RUBBER

From Equation (20) it is possible to deduce an equation of state for rubber by using the methods of the author[4] or of Kuhn as amended by Treloar[2]. However, another derivation will now be given which parallels the conven-

tional statistical methods. Making use of Boltzmann's relation, the entropy will be given by the expression:

$$S = k \ln W_{\max}. \tag{22}$$

Putting in the expression for W and making use of Stirling's approximation, we obtain from (22):

$$S = Nk \ln N - k \sum_i N_i \ln (N_i/p_i). \tag{23}$$

Taking cognizance of (9), (10), and (12) it is found that:

$$S = Nk \ln N - Nk\lambda - k\mu l^2/C. \tag{24}$$

Eliminating λ, C, and μ from (24) by use of Equations (15), (18), and (19), it is found that:

$$S = Nk \ln \alpha - Nk(\alpha^2 - 1)/2. \tag{25}$$

Equation (25) gives that portion of the entropy which can be associated with deformation effects, and is not to be regarded as the total entropy of the rubber. But just as it is possible to deduce a correct equation of state for an ideal gas by considering volume effects alone, so too an equation of state for rubber can be derived by investigating the relationship between entropy and length. Differentiating (25) with respect to length there is obtained:

$$dS = - (Nk/l_0)(\alpha - 1/\alpha)dl. \tag{26}$$

From the fundamental thermodynamic relation:

$$f = - T(\partial S/\partial l)_E \tag{27}$$

where f is the force applies, it follows that:

$$f = (NkT/l_0)(\alpha - 1/\alpha). \tag{28}$$

Equation (28) is not complete, of course, because only one dimension was considered. However, it is precisely the same equation as was derived by the author's earlier method applied to the one-dimensional problem[6]. Hence the equivalence of the two methods of attack has been demonstrated.

The extension to three dimensions can be carried out immediately. The entropy of the deformed rubber is given by the sum of expressions of type (25), using α_x, α_y and α_z as the relative stretchings in the x, y and z directions. Thus we see that:

$$S = Nk \ln (\alpha_x\alpha_y\alpha_z) - Nk(\alpha_x^2 + \alpha_y^2 + \alpha_z^2 - 3)/2. \tag{29}$$

Assuming that rubber is incompressible, it follows that $\alpha_x\alpha_y\alpha_z = 1$, which introduces some simplification in (29). If a force is applied in one direction only (say the x direction), then $\alpha_y = \alpha_z = 1/(\alpha_x)^{\frac{1}{2}}$ from which it is seen that:

$$S = - Nk(\alpha^2 + 2/\alpha - 3)/2 \tag{30}$$

where the subscript x has been dropped from α. From (30) the stretching force is readily calculated to be:

$$f = (NkT/l_0)(\alpha - 1/\alpha^2) \tag{31}$$

which result is the same as has been derived earlier[7]. The function (31) is also similar to an equation derived by Guth and James[8].

By using the methods indicated above it is also possible to show that rubber should obey Hooke's law with respect to shear. A simple shear of amount γ is obtained[9] by taking $\gamma = \alpha - 1/\alpha$ where $\alpha = \alpha_x = 1/\alpha_y$ and $\alpha_z = 1$. From (29) the entropy of shear is calculated to be:

$$S = -Nk\gamma^2/2. \tag{32}$$

Hence the shearing moment (L) will be given by:

$$L = -T(\partial S/\partial\gamma)_E = NkT\gamma. \tag{33}$$

From (33) it is seen that L is proportional to γ; in other words, Hooke's law is obeyed.

Equations (31) and (33) can be regarded as ideal equations of state for rubberlike substances. This view is justified because of the high degree of correspondence between the derivation and the limitations of Equations (31) and (33) and those of the ideal gas law. Actual samples of rubber do not obey the above-mentioned equations exactly for two principal reasons. First, the distribution functions (1) and (2) are not valid for large values of x and, second, the van der Waals interactions have been neglected in the calculations. The errors introduced thereby increase with increasing deformation. Even if exact distribution functions were used in place of (1) and (2), the equations of state so derived would not be correct for large deformations because of intermolecular attractions and repulsions.

REFERENCES

[1] Meyer, von Susich and Valko, *Kolloid-Z.* **59**, 208 (1932); Guth and Mark, *Monatsh.* **65**, 93 (1934); Kuhn, *Kolloid-Z.* **68**, 2 (1934); **76**, 258 (1936); Guth and James, *Ind. Eng. Chem.* **33**, 624 (1941); **34**, 1365 (1942); Wall, *J. Chem. Physics* **10**, 132, 485 (1942).
[2] Treloar, *Trans. Faraday Soc.* **34**, 36 (1943).
[3] Kuhn, *Kolloid-Z.* **68**, 2 (1934) **76**, 258 (1936).
[4] Wall, *J. Chem. Physics* **10**, 132, 485 (1942).
[5] See, for example, Tolman, "Statistical Mechanics", Oxford Univ. Press, **1938**, p. 79; Mayer and Mayer, "Statistical Mechanics", John Wiley & Sons, **1940**, p. 113.
[6] Wall, *J. Chem. Physics* **10**, 132 (1942).
[7] Wall, *J. Chem. Physics* **10**, 485 (1942); Treloar, *Trans. Faraday Soc.* **34**, 36 (1943).
[8] Guth and James, *Ind. Eng. Chem.* **33**, 624 (1941); **34**, 1365 (1942).
[9] Love, "Mathematical Theory of Elasticity", Cambridge Univ. Press, 2nd Ed., p. 34.

FLEX LIFE AND CRYSTALLIZATION OF SYNTHETIC RUBBER *

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The crystalline structure of stretched natural rubber has been the subject of much experimental work in the past. A great deal of this has been devoted to the more theoretical aspects, such as x-ray patterns, thermal effects, and volume change. It is now known that neither Buna-N nor GR-S has a fiber diagram when stretched and that Butyl-B and Neoprene do have such patterns.

Since the industry is now in the process of changing from natural rubber to GR-S, it is of interest to see just what this lack of crystallinity means from a compounding and performance standpoint. It is possible that many of our ideas based on rubber must change, that GR-S must be considered to be a new material, and that radical changes in formulation and construction must be made.

PHYSICAL EFFECTS OF CRYSTALLIZATION

When natural rubber is stretched, an alignment and fitting together of adjacent molecules or parts takes place which has many of the theoretical aspects of crystallization. The physical result is that the rubber becomes fibrous. It becomes stronger as it is stretched. Its resistance to rupture or tearing is increased by the very force or deformation that tends to rupture it. At the same time it becomes weaker in a direction at right angles to this. The result is that tensile strength is high whether or not a reinforcing pigment is used, and rubber may be said to be reinforced by its own crystallization.

The tearing behavior of rubber was covered extensively some years ago by Busse[1]. His work involved determining the relation between the depth of a transverse cut and the force required to rupture the strip. It was shown that, because of "semiracking", the force required to make a cut grow part way across a strip was under some conditions not sufficient to make it tear all the way across. Again, if the strip were stretched before cutting, there was a certain degree of elongation, somewhat less than the ultimate, at which the strip had to be cut three-quarters of its width to produce complete rupture; at lower elongations a much smaller cut was sufficient. This same phenomenon of semiracking was used to explain the knotting of a carbon black stock, where the tear has a strong tendency to go at right angles to any chosen direction of tear.

A totally different approach, but equally effective, was used by Cadwell, Merrill, Sloman, and Yost[2]. Rubber was flexed from various starting elongations greater than zero, with the result that flex life improved tremendously as elongation was increased, and passed through a maximum at a point somewhat below the ultimate elongation.

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This ability to resist rupture in the direction of strain is thought to be one of the greatest contributing factors to the toughness of vulcanized natural rubber. The object of this paper is to search for a similar behavior in synthetic rubber.

TEARING EXPERIMENTS

Four typical compounds were made up (Table I) and subjected qualitatively to a tear test designed to reveal any tendency toward fibering. Wide dumbbell pieces were cut with a razor longitudinally and stretched in a Cooey machine, and attempts were made to continue the splits by tearing manually. Other pieces were stretched, then razor-cut longitudinally, and tearing was attempted.

TABLE I

FORMULATION OF COMPOUNDS

Natural rubber	100.00	....	....	....
Buna-N	....	100.00	....	....
GR-S	....	....	100.00	....
Butyl B-1.45	....	....	....	106.50
Channel black	50.00	50.00	50.00	60.00
Stearic acid	3.00	2.00	2.00	3.00
Pine tar	3.00	....	....	....
SDO No. 10 (Barrett)	....	3.00	3.00	....
Medium process oil	....	....	....	3.00
Zinc oxide	5.00	5.00	5.00	....
Sulfur	3.00	2.00	2.00	....
Mercaptobenzothiazole	1.25	1.50	1.50	....
Tetramethylthiuram disulfide	....	....	....	1.00
Total	165.25	163.50	163.50	173.50
Cure, min. (° F)	70 (260)	50 (260)	50 (290)	70 (310)

Still other pieces were stretched, then punctured with a pin, and attempts made to force the pin along the strips longitudinally and thereby split them.

These experiments were conducted at elongations from about 50 per cent of the ultimate values to the ultimate values. In the case of natural rubber, splitting was comparatively easy. Butyl-B behaved the same way, but splitting was a little more difficult. Buna-N and GR-S could not be split; in fact they frequently tore completely across as soon as a longitudinal cut or a pinhole was made (Table II).

TABLE II

RESULTS OF TEARING EXPERIMENTS

	Natural	Buna N	GR-S	Butyl B-1.45
Min. elongation allowing split (approx.) (%)	350	...	...	700
Ultimate elongation (%)	575	450	450	850
Splitting	Easy	No	No	Possible

In this respect, then, rubber and Butyl-B are in one class, while Buna-N and GR-S are in another.

FLEXING EXPERIMENTS

An experiment was designed to show the effect of flexing amplitude and starting elongation on flex life—in other words, to show whether or not flex life was greater when the test-piece remained within the range of elongation where crystallization could occur.

Ring-shaped test-pieces were flexed on a machine designed by G. J. Albertoni[3]. The speed was 550 cycles per minute. It was possible to use amplitudes as low as 25 or as high as 400 per cent. Starting elongations were limited on the low side by the permanent set of the test-piece. At low amplitudes the maximum elongation was limited by the machine as follows:

Amplitude (%)	25	75	125
Max. elongation (%)	115	90	65

At amplitudes of 150 per cent and above, the starting elongation was limited on the high side only by the nature of the stock under test. A further limitation was introduced that in most cases no run was made beyond 800 kilocycles, corresponding to 24 hours.

Table III and Figure 1 show several curves for natural rubber. The existence of a peak is marked. It is possible that the first few increments of initial elongation make flex life poorer, particularly at the higher amplitudes, but

TABLE III

FLEX LIFE OF NATURAL RUBBER AND BUTYL B-1.45[a]

Minimum elongation (%)	Flex life of natural rubber at amplitude of: 150%	200%	250%	300%	350%	400%	Flex life of Butyl at amplitude of 400%
				Kilocycles			
0	Too much set	...	...	...	...	...	
10	23	...	...	...	1.53	...	
25	21	...	...	2.4	0.91	0.57	Too
50	288	...	...	...	0.95	0.38	much
75	(2120+)	...	...	3.9	0.65	0.25	set
100	(450+)	...	...	...	0.77	...	
125	...	...	...	33.2	0.88	0.64	13.3
150	...	...	...	...	4.7	0.65	16.6
175	...	...	...	221[a]	9.7	...	24.2
200	...	...	...	...	6.5	...	22.6
225	...	...	...	...	0	...	20.8
250	...	...	...	...	...	...	30.6
275	...	...	...	0	...	...	38.0
300	...	...	...	...	...	...	72.7
325	...	...	0	...	...	...	...
350	...	...	...	...	...	...	(800%)
375	...	17	...	...	...	...	...
400	...	...	...	...	...	...	(800+)
425	...	...	...	...	...	...	(800+)
450	12	...	...	...	...	...	...
475	...	...	...	...	...	...	(800+)
500	...	...	...	...	...	...	...
525	...	...	...	...	...	...	71
550	...	...	...	...	...	...	0

[a] For example, the figure 221 means that strips flexed from 175 to 475% had a life of 221,000 cycles, or about 6.5 hours.

soon there is a sharp rise in flex life, and finally a reduction again as the ultimate elongation is approached. The exact location of the peaks has not been determined, but it appears that all should occur at maximum elongations between 400 and 550 per cent.

Butyl-B has a similar behavior (Table III and Figure 2). Its peak is just as sharp as natural rubber, but falls at a higher elongation, possibly at a maximum elongation of 800 per cent.

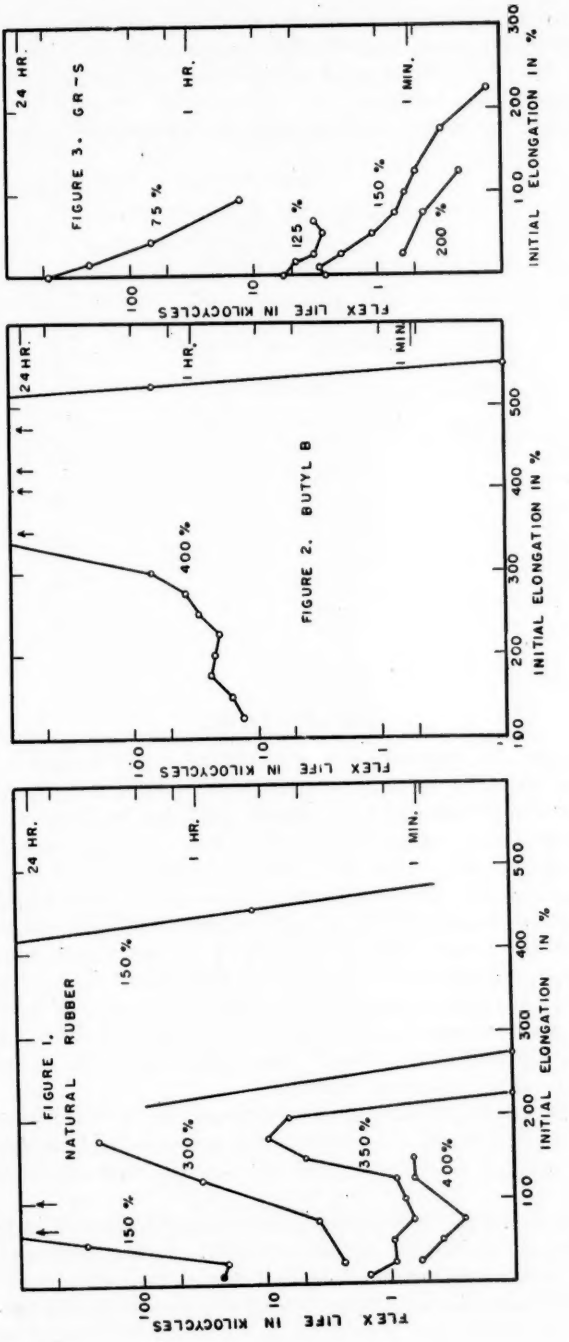
FIGURE 3. GR-S
24 HR.
1 HR.
1 MIN.
75 %
125 %
150 %
200 %
FLEX LIFE IN KILOCYCLES
INITIAL ELONGATION IN %
FIGURE 2. BUTYL B
24HR.
1 HR.
1 MIN.
400 %
FLEX LIFE IN KILOCYCLES
INITIAL ELONGATION IN %
FIGURE 1.
NATURAL RUBBER
24 HR.
1 HR.
1 MIN.
150 %
300 %
350 %
400%
FLEX LIFE IN KILOCYCLES
INITIAL ELONGATION IN %

GR-S shows no evidence of a peak (Table IV and Figure 3). All curves, within experimental error, start to fall immediately as initial elongation is increased above zero. The decline as the breaking elongation is approached is gradual rather than abrupt.

Again rubber and Butyl-B are in one class, while GR-S is in another.

TABLE IV

FLEX LIFE OF GR-S

Minimum elongation (%)	Flex life (kilocycles) at amplitude of				
	25	75	125	150	200
0	...	453	5.8	2.6	...
8.4	...	...	...	2.9	...
15	(800+)	214	4.6	...	...
25	...	...	3.2	2.0	0.63
40	(800+)	67	...	...	...
50	...	...	2.8	1.1	...
65	(800+)	...	3.2	...	...
75	...	...	...	0.72	0.43
90	...	13	...	...	...
100	...	...	...	0.61	...
115	...	...	...	...	...
125	...	...	...	0.50	0.22
150	...	...	...	...	...
175	...	...	...	0.31	...
200	...	...	...	...	...
225	...	...	...	0.13	...
250	...	...	...	...	...
275	...	...	...	...	...

IMPLICATIONS

These experiments illustrate a type of behavior or a tendency which has a bearing on performance both in service and in laboratory tests. When a typical rubber tire is run under conditions that can produce tread cracking, it is found that many cracks are started before the first cracks have grown very large. On the other hand, since crack growth in a GR-S tire is not retarded by fibering, the first cracks may grow quite large before many are formed. The most successful flex tests for rubber in this laboratory have been those in which the crack has been permitted to start itself, such as the De Mattia and the perforated (cut round hole) strip test. These tests have not been successful with GR-S, but if either test-piece is cut or nicked before test, it becomes a good measure of cut growth. A natural rubber test-piece so nicked or cut will frequently "knot", and cut growth will be retarded until other points of failure have been started.

Lacking the benefit of fibering, the compounding of GR-S becomes a more delicate job than that of natural rubber. It is not expected that any compounding steps will produce fibering. Improved flex life must be obtained in spite of this lack.

The use of carbon black has been quite generally adopted in GR-S. This was done primarily to increase tensile strength. It was necessary because of the lack of crystal reinforcement in GR-S and its consequent low tensile strength. Its action is thought to be exactly the same as it is in natural rubber; but since natural rubber can crystallize, it is already well bound together, and the possible increase in tensile strength is not so great as it is with GR-S.

Obviously, the most highly reinforcing black permitted by heat build-up and processing should be used.

In polymer research, vigorous efforts should continue to get some degree of crystallization into the government tire rubber. It is already present in two synthetics. If this can be done and the other fine properties of GR-S still be maintained, it is predicted that flex life will be greatly improved and that "gum" stocks will be possible.

ACKNOWLEDGMENT

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REFERENCES

[1] Busse, *Ind. Eng. Chem.* **26**, 1194 (1934); RUBBER CHEM. TECH. **8**, 122 (1935).
[2] Cadwell, Merrill, Sloman and Yost, *Ind. Eng. Chem. Anal. Ed.* **12**, 19 (1940); RUBBER CHEM. TECH. **13**, 304 (1940).
[3] Albertoni, G. J., Goodyear Tire and Rubber Co. laboratories.

HEATS OF VULCANIZATION OF SYNTHETIC RUBBERS *

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A previous paper[1] reported that the heat of reaction between Hevea rubber and sulfur was measured by following the temperature at the center of a rubber cylinder during vulcanization. It was found that with all percentages of sulfur used, there is evolution of heat. Below about 2 parts of sulfur per 100 of rubber, the heat evolved is relatively small. Above this region the evolution becomes progressively larger, and increases as the percentage of sulfur increases.

It was suggested that this might be explained by assuming two reactions between sulfur and rubber. The first, which is the principal reaction at low sulfur percentages, forms solft vulcanized rubber, and is accompanied by little or no heat evolution. Above the low sulfur region, a second reaction predominates which forms ebonite and produces a relatively large quantity of heat.

By the use of organic accelerators, the rate of formation of soft vulcanized rubber is greatly increased, but the rate of formation of ebonite is practically unaffected. By accentuating the soft rubber reaction, the two reactions may be more completely separated. The presence of accelerators decreased the heat evolved at a given percentage of sulfur, an effect which would be predicted from the theory of two distinct reactions.

The two reactions may be still more completely separated by means of selenium. Although this material will form soft vulcanized rubber, it differs from sulfur in its inability to produce ebonite. Since vulcanization of rubber with selenium produced no detectable heat evolution, further support is given to the theory of two reactions.

HEAT EVOLUTION

The present paper is concerned with the heat evolved during the vulcanization of synthetic rubbers. Buna-S, Buna-N, Butyl, and Neoprene-GN were investigated.

The apparatus and procedure were similar to that previously described[1]. A cylinder of synthetic rubber compound was prepared by rolling a milled sheet of appropriate dimensions. A copper-constantan thermocouple junction was placed in the center of the cylinder during its formation about 40 mm. from the base. The cylinder was wrapped in cellophane and forced into a 38 × 200 mm. Pyrex test-tube. The diameter of the rubber clyinder was so adjusted that good contact was made between the walls of the test tube and the rubber compound. The test-tube, together with the other thermocouple junction, was then placed in a 2-liter flask containing condensing aniline vapor (184.4° C). The temperature differences between the center of the rubber mass and the aniline vapor were measured at approximately 1-minute intervals.

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By plotting these temperature differences against time, a curve is obtained whose shape depends on the amount of heat evolved. Typical heating curves are shown in Figure 1. The active curve is plotted from data obtained during the heating of a Buna-S (Firestone GR-S) compound containing 6 parts of sulfur per 100 of Buna-S. At the conclusion of this heating, the reaction between the Buna-S and the sulfur is complete and the material is thermally inactive. A blank heating curve may then be obtained by cooling and again heating in aniline vapor. The maximum temperature difference between the active and blank curves is taken as a measure of the heat evolved.

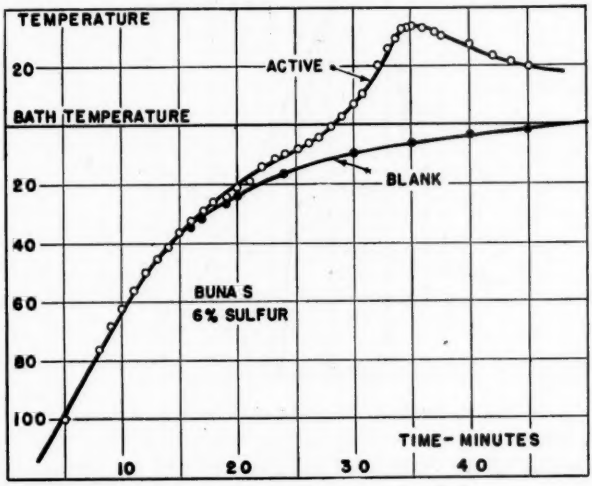

FIG. 1.—Typical heating curves.

A more convenient method of determining this maximum temperature difference makes use of the logarithmic nature of heating curves. If a thermally inactive mass is heated by a constant temperature source, the logarithm of the unaccomplished temperature change at any point within the mass is a straight-line function of time. Deviation from a straight-line function indicates thermal activity of the sample.

In Figure 2 a semilogarithmic plot of the blank heating curve is shown to be a straight line. The first portion of the heating curve of the active sample is identical with the straight line, indicating that no heat is being evolved. At approximately 25° C below the bath temperature, the active curve begins to deviate from the straight line and thus shows the evolution of heat. A blank heating curve for any particular composition may, therefore, be obtained by plotting the experimentally determined temperatures for a thermally active sample on a logarithmic scale and extrapolating the straight-line portion. A transfer of the extrapolated line to a linear plot, such as Figure 1, allows the evaluation of the temperature differences between the active heating curve and its blank.

If the heat transferred between the aniline vapor and the sample were the same as that for the blank, the calories evolved per gram of rubber could be calculated from the maximum temperature difference and the specific heat of the sample. However, the amount of heat transferred from the aniline vapor

into the sample decreases as the amount of heat evolved increases. For this reason there is a small positive error which becomes greater with increasing heat evolution. This error is believed to be small since the reaction takes place within a short time.

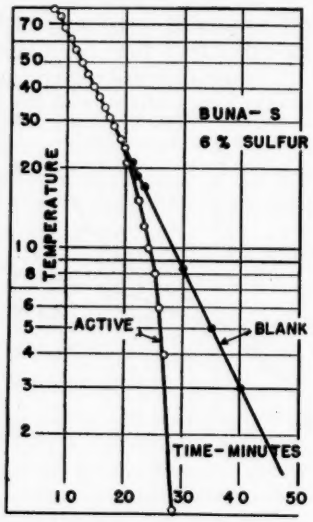

FIG. 2.—Semilogarithmic plot of typical heating curve.

Neglecting the above error, the calories evolved per gram of rubber may be calculated from the following equation:

$$\text{calories per gram} = \frac{(S)(\text{max. } \Delta T)}{f}$$

where S = specific heat of compound
max. ΔT = maximum difference between active and blank curves, ° C
f = fraction of rubber in compound.

The specific heat values used were: organic materials, 0.5; carbon black, magnesium oxide, and sulfur, 0.2; zinc oxide, 0.1. Inaccuracies in these values are reflected in the absolute values for heats of vulcanization, but the relative values are not affected.

BUNA-S

The Buna-S (Firestone GR-S) was a copolymer of approximately 75 parts butadiene and 25 parts styrene. Four types of Buna-S compounds were investigated:

	A	*B*	*C*	*D*
Buna-S	100	100	100	100
Carbon black (Micronex)	...	...	50	10–60
Zinc oxide	...	5	5	5
Stearic acid	...	1	1	1
Santocure (accelerator)	...	1	1	1
Sulfur	2–10	2–10	2–10	10

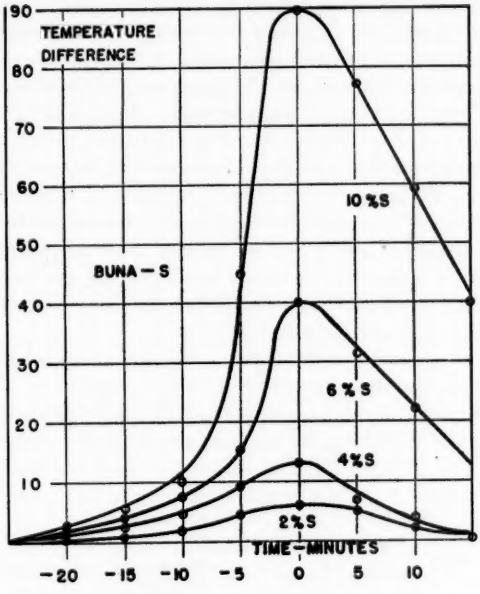

FIG. 3.—Temperature differences between heating curves for active and blank samples.

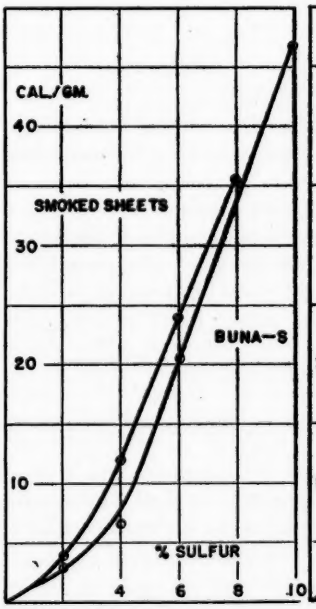

FIG. 4.—Comparison of heat evolution of Buna-S and natural rubber.

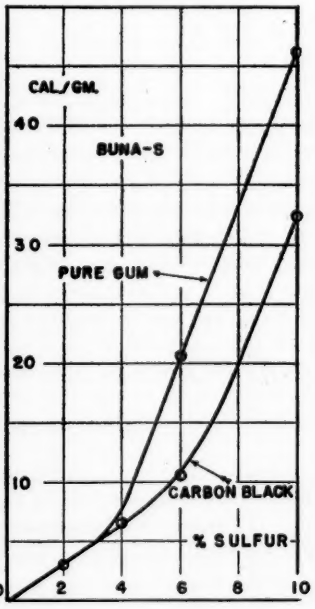

FIG. 5.—Effect of carbon black on heat evolution of Buna-S.

The temperature differences between the heating curves for the active and blank samples are shown in Figure 3 for various unaccelerated Buna-S-sulfur mixtures. The curves are plotted arbitrarily so that all maximum temperature differences occur at the same time. The calories evolved per gram of Buna-S, calculated from the maximum temperature difference values, are plotted against percentage sulfur in Figure 4. For comparison, the values for smoked sheet rubber previously obtained[1] are also given. The curve for the accelerated Buna-S compounds (type *B*) is not given, since it was nearly identical with the unaccelerated type. This may be contrasted with values for smoked sheet in which case the addition of accelerators lowered the heat of vulcanization. The heat of vulcanization curve for Buna-S is similar to the curve for natural rubber. Both curves show a definite upward bend in the low-sulfur region, which indicates the presence of two reactions.

The addition of carbon black to Buna-S appears to lower the heat of vulcanization in the region above 4 per cent sulfur (Figure 5). Below this point, the values are identical for both the pure-gum and carbon black compounds. This effect might be explained by an increase in heat conductivity caused by the carbon black, or a change in the amount of heat evolved, or both. If the difference between the two curves is due to increased heat conductivity, separate

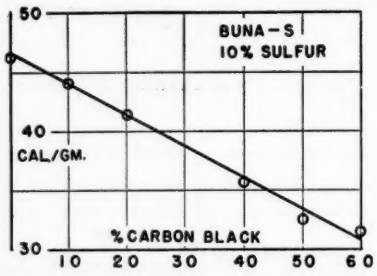

FIG. 6.—Effect of varying amounts of carbon black on heat evolution of Buna-S.

curves should exist in the 0 to 4 per cent sulfur region. Since they are identical in this region, it is believed that a change in heat conductivity is not a sufficient explanation. The curves suggest that the presence of carbon black in Buna-S decreases the heat of vulcanization in the 4–10 per cent sulfur region.

The effect of varying the amount of carbon black in a Buna-S compound containing 10 per cent sulfur is shown in Figure 6. The calories evolved decrease linearly with increase in percentage of carbon black.

BUNA-N (HYCAR OR-15)

This synthetic rubber is a copolymer of butadiene and acrylonitrile. Its heat of vulcanization was studied in a series of typical compounds containing carbon black. (Pure-gum compounds proved to be insufficiently plastic to be adapted to the procedure used.) The formula follows:

Hycar OR-15	100	Stearic acid	1
Carbon black (Micronex)	35	Benzothiazyl disulfide	1.5
Dioctyl phthalate	20	Sulfur	2–14
Zinc oxide No. 550	5		

Heats of vulcanization are plotted in Figure 7, together with those obtained for smoked sheet rubber. The rapid change in slope of the curve for Hycar OR-15 does not occur until near 10 per cent sulfur, compared with the change at about 2 per cent sulfur for natural rubber. In the region from 4 to 10 per cent sulfur, Hycar OR-15 shows a relatively small heat of vulcanization. This

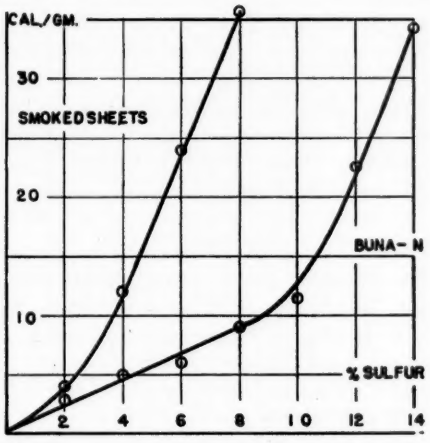

FIG. 7.—Comparison of heat of evolution of Buna-N and natural rubber.

may be taken as an indication that the ebonite reaction in this region does not occur so readily in Hycar OR-15 as it does in natural rubber.

BUTYL RUBBER (B-1.45)

Butyl is a copolymer of a diolefin and isobutylene. The percentage of diolefin is adjusted in the material used (B-1.45) so that the double bonds available for vulcanization are approximately 1.5 per cent of those available in natural rubber. If one sulfur atom reacts per double bond, the maximum amount that can combine will be 0.72 part of sulfur per 100 of Butyl rubber. If the heat of reaction is similar to that of natural rubber, an excess of sulfur will produce about 1 calorie per gram of Butyl. Approximately this amount of heat was evolved by the following compounds:

Butyl rubber	100	100	100
Zinc oxide No. 550	5	5	5
Stearic acid	2	2	2
Carbon black (Micronex)	...	...	40
Tetramethylthiuram disulfide	...	1	1
Mercaptobenzothiazole	...	0.5	0.5
Sulfur	5	5	5

Butyl rubber may also be vulcanized with *p*-quinone dioxime and lead peroxide. The study of this reaction, however, is complicated by a strongly exothermic reaction between *p*-quinone dioxime and lead peroxide. A correction for the heat of this side reaction was obtained by determining the heat evolved by these vulcanizing agents when heated in Vistanex. The latter material has substantially the same structure as Butyl rubber but no appreciable unsaturation.

The following table gives the compound formulas and their respective heats of vulcanization:

Butyl rubber	100	...
Vistanex	...	100
p-Quinone dioxime	6	6
Lead peroxide	10	10
Zinc oxide	5	5
Stearic acid	2	2
Heat evolved (cal. per gram)	24	18

The difference between these values (6 calories per gram) may be taken as an approximation of the heat evolved by the reaction between Butyl rubber and the vulcanizing agents. This value is considerably higher than 1 calorie per gram produced in the sulfur vulcanization.

NEOPRENE

In contrast to the materials previously discussed, Neoprene (polychloroprene) will vulcanize in the absence of other materials. It is common practice, however, to use metallic oxides in Neoprene compounds. Heats of vulcanization have been determined for Neoprene-GN, alone and with zinc and magnesium oxides. Unusual care was taken by use of low temperatures to avoid any cure during mixing operations.

The following table gives compound formulas and their respective heats of vulcanization:

		E	
Neoprene-GN	100	100	100
Light calcined magnesia	...	4	4
Stearic acid	...	0.5	0.5
Zinc oxide No. 550	...	5	10
Heat evolved (cal. per gram)	15	12	12

The heat of vulcanization of Neoprene alone is appreciable and corresponds to a value for smoked sheet rubber containing 4.5 per cent sulfur. The addition of 5 per cent zinc oxide and 4 per cent magnesia definitely lowers the heat evolution. The amount of heat evolved is not changed by increasing the zinc oxide to 10 per cent.

SUMMARY

1. The heats of vulcanization for natural rubber and Buna-S are nearly equal. The data for both materials indicate two different chemical reactions during vulcanization. At low sulfur percentages, the principal reaction forms soft vulcanized rubber and is accompanied by little or no heat evolution. Above the 2 per cent sulfur region, a second reaction predominates, forming hard rubber and producing a relatively large quantity of heat.

2. The presence of an accelerator (Santocure) in Buna-S has little, if any, effect on heat of vulcanization.

3. The addition of carbon black to Buna-S lowers the heat of vulcanization in the region above 4 per cent sulfur. The calories evolved in a 10 per cent sulfur compound decrease linearly with percentage of carbon black.

4. The heats of vulcanization of Buna-N (Hycar OR-15) indicate the presence of two chemical reactions. Unlike natural rubber and Buna-S, the ebonite reaction does not predominate until the sulfur concentration is raised above 10 per cent.

5. The heat of vulcanization of Butyl rubber with sulfur is equal to the heat evolved with natural rubber containing 0.6 per cent sulfur. If one sulfur atom reacts per double bond, the maximum amount combining would be 0.72 per cent sulfur. During the vulcanization of Butyl rubber with *p*-quinone dioxime and lead peroxide, a large amount of heat is evolved by a side reaction between the vulcanizing agents. The reaction involving the Butyl rubber produces about 6 calories per gram, a considerably higher value than the 1 calorie produced by sulfur vulcanization.

6. The heat of vulcanization of Neoprene-GN without added agents corresponds to a value for smoked sheet rubber containing 4.5 per cent sulfur. The addition of zinc oxide and magnesia decreases the heat of vulcanization.

REFERENCE

[1] Blake, *Ind. Eng. Chem.* **26**, 1283 (1934); RUBBER CHEM. TECH. **8**, 112 (1935).

TEMPERATURE COEFFICIENT OF VULCANIZATION OF BUNA-S *

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Temperature coefficient of vulcanization may be defined as the increase in time of vulcanization necessary to produce a given property in the vulcanizate per unit range of temperature decrease, the latter being taken usually as either 10° F or 10° C. Coefficients of vulcanization for natural rubber stocks have been determined by several investigators[1]. Although the data vary somewhat with the worker and with the stock investigated, the general range of temperature coefficients is close to 2.0 per 10° C. This is regarded as evidence of the chemical nature of the vulcanization reaction[2]. The values obtained from physical test data do not always agree with those from combined sulfur analyses. This has been interpreted as an indication that the chemical reaction between the rubber and sulfur is not a simple bimolecular one, and that the rate of change of physical properties is not directly related to the rate of chemical combination of rubber and sulfur.

A number of studies were published recently on the effect of variables on the vulcanization of Buna-S (now called GR-S in the United States) and on the properties of the resulting vulcanizates[3]. In addition, compounding reports have been issued by manufacturers of rubber chemicals, as well as confidential reports submitted to the Rubber Director's office by rubber manufacturers. None of the published investigations, however, have been concerned with the determination of numerical relations among the properties of vulcanizates obtained at various temperatures. The properties of Buna-S vulcanizates differ markedly from those of rubber in certain characteristics, while possessing certain similarities in others[4].

The only published mention of the effect of temperature on Buna-S stocks was in a release from the office of the Rubber Director, giving tables for conversion of cure to a standard temperature[5]. These tables are based on a temperature coefficient of 1.43 per 10° F. The source of this information is not available, however.

EFFECT OF TEMPERATURE

This investigation was devoted to a study of the effect of temperature on the rate of chemical combination as well as the rate of change of physical properties of three related Buna-S recipes (Table I).

They consisted, respectively, of a pure-gum control, a tread type reinforced with an impingement-type carbon black, and a mechanical-goods type containing a fine thermal black. The remainder of the recipe was kept constant, and the sulfur was varied from 1 to 5 per cent (on the polymer); the stocks

* Reprinted from *Industrial and Engineering Chemistry*, Vol. 36, No. 1, pages 33–36, January 1944. This paper was presented before the Division of Rubber Chemistry at its semiannual meeting in New York, October 5–7, 1943.

TABLE I

STOCK RECIPES

Buna-S	100	100	100
Zinc oxide	5	5	5
Stearic acid	1	1	1
Dibenzothiazyl disulfide	1.5	1.5	1.5
Bardol (softener)	5	5	5
Channel black	...	50	...
Fine thermal black	...	...	60
Sulfur	Variable	Variable	Variable

contained 1, 2, 3, and 5 per cent of added sulfur, respectively. Each of the twelve stocks was then cured for 20, 50, 80, 110, and 140 minutes at each of four temperatures (270°, 280°, 290°, and 300° F). In this way the data were directly comparable with respect to the three variables—time, temperature, and sulfur content.

This arbitrary choice of conditions led to pronounced overcures in some cases and pronounced undercures in others; still other stocks failed to reach an optimum cure in the time employed. Constancy of the accelerator content led to poor sulfur-accelerator ratios in some cases[6]. However, an extension of the problem to include all the desirable data would have been beyond the scope of this investigation.

The general procedures were those of the A. S. T. M.[7]. To eliminate any variables in the polymer itself, a large batch, sufficient for the entire problem, was well blended in a Banbury mixer, and all ingredients except the carbon black and sulfur were incorporated at this time. This master batch was divided into three portions. One portion was retained for use as the pure-gum stock; the other two were blended with the requisite portions of pigment and stored before use. The sulfur was incorporated into each stock shortly before use. The proper quantity of sulfur was weighed on an analytical balance and milled into the master batch of stock on a 10-inch mill.

The temperature of the platens in the steam-heated presses was checked with a calibrated thermometer and a mercury block. The cured stocks were stored between sheets of heavy parchment paper before testing. Stress-strain properties were determined by the A. S. T. M. procedure. Total sulfur was determined by the Cheyney modification of the A. S. T. M. method[8]. Free sulfur was determined by a semimicro modification of the method of Oldham, Baker, and Craytor[9]. Combined sulfur was calculated as the difference between total sulfur and free sulfur, as determined analytically except for modifications noted below. For comparative purposes, the combined sulfur data for all three stocks were calculated as coefficient of vulcanization (percentage of sulfur combined with 100 parts polymer as compounded).

The original polymer batch contained an appreciable quantity of sulfur (0.25 per cent). The presence of this sulfur and an indication of its origin were considered previously[10]. For the calculations reported here, this "blank" sulfur was assumed to be present in the final vulcanizate entirely in the combined form; the analytical data were corrected accordingly. It was likewise necessary to correct for the sulfur originating in the accelerator, which is 38.57 per cent of the accelerator content, or 0.58 per cent sulfur per 100 parts polymer in the stocks investigated; this type of sulfur was assumed to undergo no change during vulcanization. Neither of these assumptions may be entirely justified. However, a considerably more refined analytical technique, as well as a larger

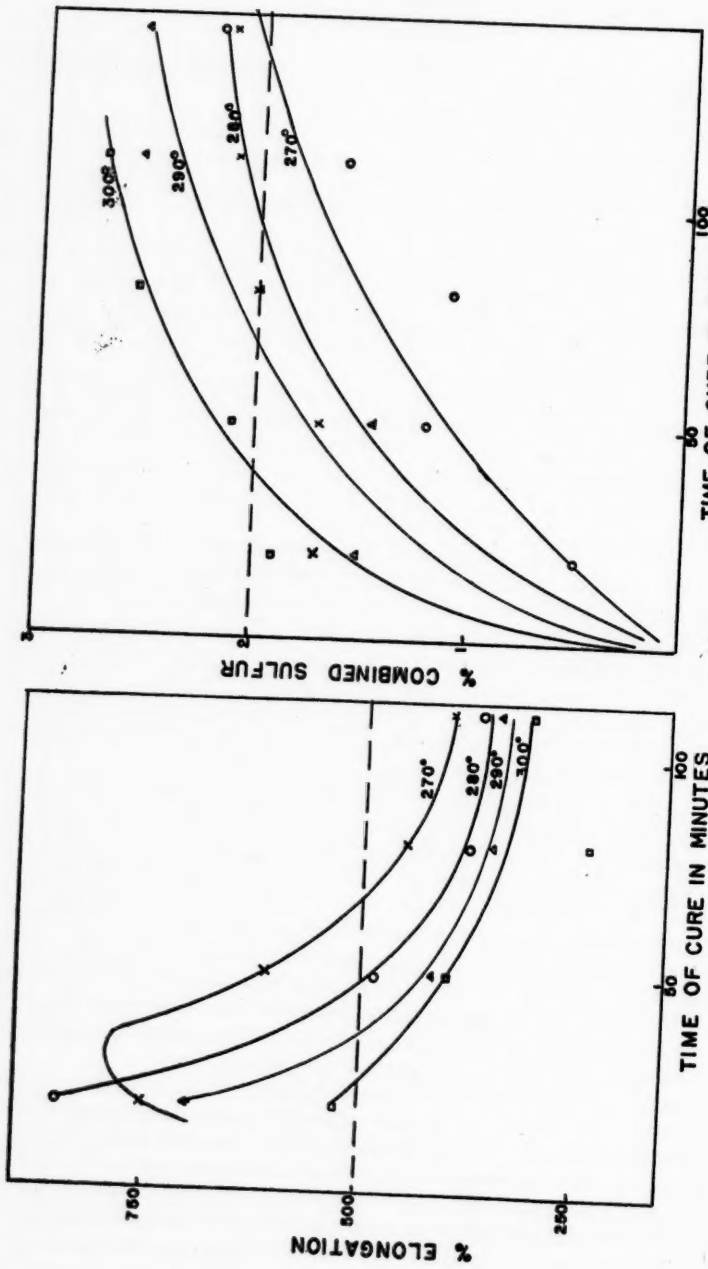

FIG. 1.—Typical elongation-time curves (soft-black stock, 3 per cent added sulfur).
FIG. 2.—Typical combined sulfur-time curves (pure-gum stock, 3 per cent added sulfur).

amount of experimental work, would be necessary to evaluate the changes in character of these two types of sulfur during vulcanization.

TYPES OF CURVES

The experimental data were plotted against time of cure in the standard way. Inclusion of all forty-eight sets of curves would be impossible, so only the significant data are presented here.

The general method of calculating temperature coefficient is based on plotting the logarithm of the time necessary to reach some standard property against temperature; the temperature coefficient is then the antilogarithm of the slope of the resulting curve. A more convenient method is to plot time against temperature on semilogarithm coördinates; the temperature coefficient may then be obtained by the direct ratio of the two time values taken from the straight line obtained.

The selection of standard properties for the various stocks required some experimentation. Park, Sandstrom, Morris, and Eliel felt that modulus (load at a fixed elongation) was more reproducible for natural rubber than either ultimate tensile strength or elongation. Attempts to use modulus measurements for these calculations, however, failed to achieve satisfactory results. In both the pure-gum and soft-black stocks, but especially in the former, the modulus was so low that the error introduced by this procedure was rather large. The channel-black stocks had moduli of sufficient magnitude, but when plotted, several of the points failed to fall on or near the necessary straight line.

The ultimate elongation-time curves finally chosen as standard had the best-defined shape of any of those investigated. In all stocks the ultimate elongation rapidly reached maximum values (in some stocks the maxima were already past in the shortest cures) and then decreased almost as rapidly, finally leveling off at rather constant values. Actual trials showed that the selection of arbitrary elongation values on the relatively steep portions of the descending part of the curves led to satisfactory results. It is considered likely that the ascending portions of the curves might have proved fully as useful, but these portions were missing in a number of the plots. Furthermore, the relative errors in reading time values in these early portions of the curves are considerably greater. Figure 1 shows a typical set of elongation-time curves; the dotted line illustrates the standard property chosen.

In this connection, the Government memorandum[5] referred to stated that good elongation is the most important characteristic of GR-S tread compounds. Also, elongation was employed in the form of the well-known T-50 test in the investigation of Gerke[11] on the effect of reclaim on temperature coefficient. Here it showed good agreement with results obtained from modulus and free sulfur data.

There was no similar choice of properties for the analytical data. It was necessary to choose some arbitrary percentage of combined sulfur which was within the ascending portions of the curves over the entire temperature range studied. Figure 2 illustrates a family of these combined sulfur-time curves, with the standard property chosen in this case.

Table II lists the values obtained by this graphical method for the various standard properties, with the property used for each determination. The corresponding log time-temperature plots are given in Figure 3. Table III lists the temperature coefficients obtained from the slopes of these curves.

The values for 10° C were calculated from those for 10° F, using the relationship: $K_F^{1.8} = K_C$.

While an effort was made to choose standard properties that would yield satisfactory straight lines, those chosen are not the only ones which would

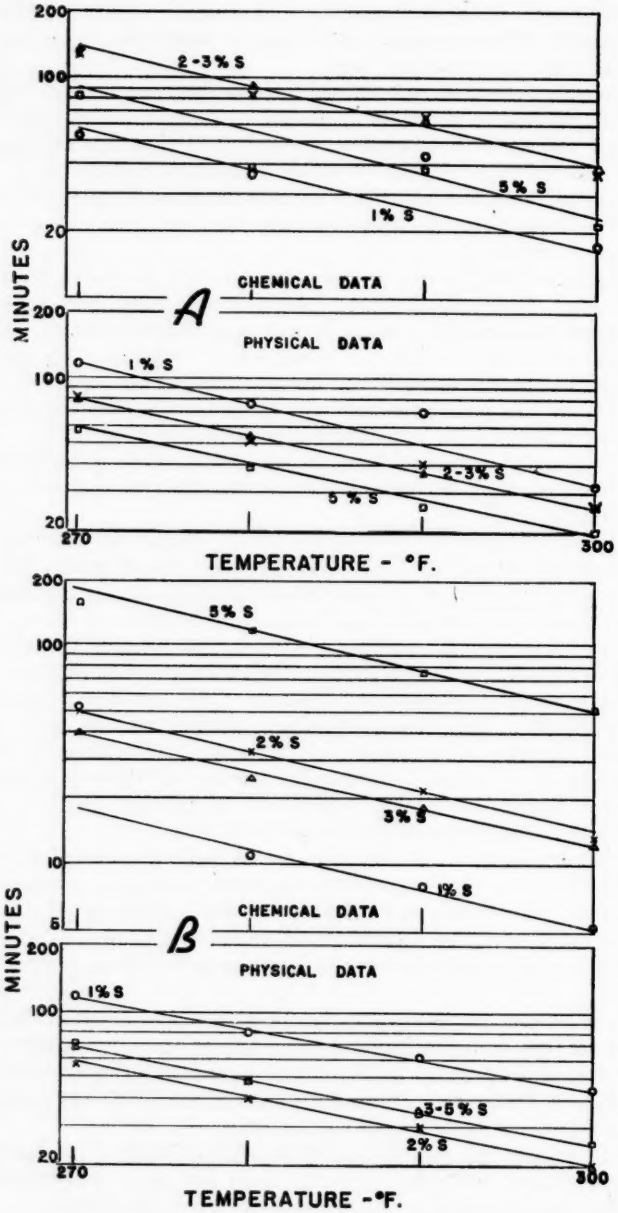

FIG. 3.—Log time-temperature curves. (*A*) Pure gum stocks, (*B*) soft black stocks.

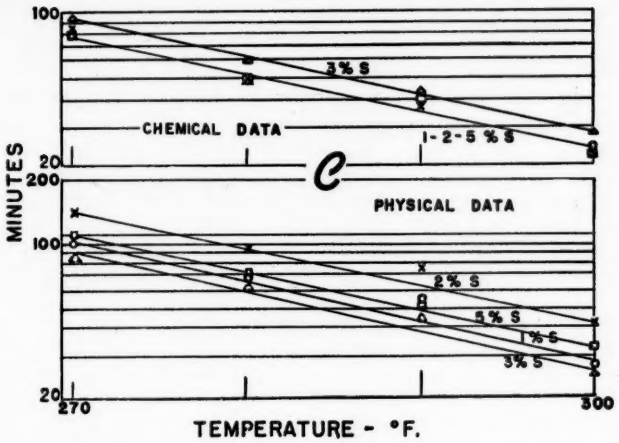

FIG. 3. *continued*—Log time-temperature curves. (*C*) channel black stocks.

yield the desired results. For instance, Figure 4 gives curves obtained with 600 and 800 per cent elongation, respectively, as the standard properties. The agreement is well within the limits of experimental error. The use of modulus instead of elongation in the cases where the modulus values show good agreement with one another yields values of the same order of magnitude; this is illustrated for a typical stock in Figure 5.

Accuracy of values reported.—The final value in each case is obtained by a combination of two graphs. In some of these the points fall almost exactly on the curve, and define the latter with considerable accuracy. In others

TABLE II

TIMES TO REACH STANDARD PROPERTIES

Percentage sulfur added	Temp., (° F)	Pure-gum stocks (min.)		Soft-black stocks (min.)		Channel-black stocks (min.)	
1		600% E[a]	0.25% S	800% E	0.25% S	600% E	0.50% S
	270	116	53	116	54	100	80
	280	76	37	80	11	72	50
	290	70	45	63	8	58	40
	300	32	18	44	4	30	23
2		600% E	1.00% S	700% E	1.00% S	450% E	1.00% S
	270	81	128	57	60	140	82
	280	53	85	40	34	98	50
	290	41	66	30	20	80	37
	300	26	38	20	12	57	22
3		500% E	2.00% S	500% E	1.50% S	450% E	2.00% S
	270	80	134	69	40	87	94
	280	55	93	47	25	65	60
	290	37	64	36	18	47	43
	300	26	40	20	12	27	28
5		500% E	3.00% S	350% E	4.50% S	250% E	3.50% S
	270	58	82	70	160	110	80
	280	39	39	47	102	74	50
	290	26	39	35	76	54	40
	300	20	24	25	50	36	22

[a] E = elongation.

TABLE III

TEMPERATURE COEFFICIENTS

Percentage sulfur added	Physical		Chemical	
	10° F	10° C	10° F	10° C
	Pure-gum stocks			
1	1.51	2.09	1.45	1.97
2	1.45	1.95	1.49	2.04
3	1.45	1.95	1.49	2.04
5	1.44	1.93	1.52	2.13
Average	1.46	1.98	1.49	2.05
	Soft-black stocks			
1	1.42	1.88	1.52	2.07
2	1.43	1.90	1.53	2.17
3	1.44	1.92	1.47	2.00
5	1.44	1.92	1.47	2.00
Average	1.43	1.91	1.50	2.07
	Channel-black stocks			
1	1.47	2.00	1.48	2.03
2	1.45	1.94	1.48	2.03
3	1.47	2.00	1.51	2.09
5	1.44	1.93	1.48	2.03
Average	1.46	1.97	1.49	2.05
Average for all stocks	1.45	1.95	1.49	2.06
Govt. figure[5]	1.43	...	...	...
Natural rubber with same accelerator[12]	1.50	2.00	1.52	2.08

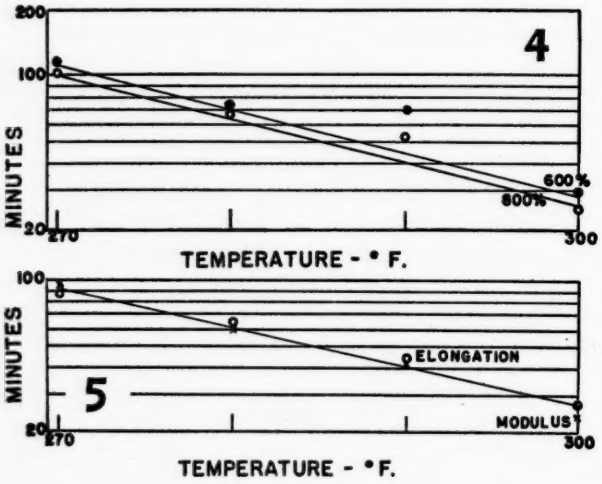

FIG. 4.—Curves obtained with 600 and 800 per cent elongation as standard (pure-gum stock, 1 per cent added sulfur).

FIG. 5.—Comparison of modulus and elongation values (channel-black stock, 3 per cent added sulfur).

there is some variation, and the investigator is forced to exercise some judgment in selecting the proper path for the curve. In the log time-temperature curves, which tend to average out some of the variations of the original experimental ones, a difference of 0.01 in the slope of the curve is relatively easy to obtain. This leads to a difference of 0.04–0.05 in the temperature coefficient

calculated from it, or about 2.5 per cent variation in the absolute values. In a semilog plot such as those reported here, the error may be slightly less but varies considerably, depending upon which portion of the line is used for the determination. The higher values give coefficients with greater accuracy, but these values are more difficult to read from the semilogarithm plot with accuracy. As a result the error tends to average out over the entire range. The over-all error is probably within ±5 per cent and the values are considered accurate to this extent.

COMPARISON WITH OTHER DATA

Comparison of the data with previously reported values for natural rubber stocks emphasizes the remarkable agreement in the magnitudes of the values obtained. There is evidently a close similarity between the mechanisms of vulcanization of the two elastomers, at least in so far as the effect of temperature is concerned. Agreement with the values of Morris[12], who used the same accelerator, is unusually good.

Although similar temperature coefficients were obtained from both physical and chemical data, at any given temperature the rate of chemical combination of sulfur and polymer is not directly related to the rate of change of physical properties. The combined sulfur approaches a limiting value with no further change, whereas a property such as ultimate elongation goes through at least three types of change: (1) rapid increase to a maximum, (2) relatively rapid decrease from this value, and (3) leveling off to a fairly constant value.

Another interesting feature of these results is the fact that, within the limits of experimental error, the same values were obtained in the presence or absence of reinforcing pigment. This may be regarded as evidence, although not conclusive proof, that the mechanism of reinforcement bears no direct relation to that of vulcanization.

Unlike much of the reported data for natural rubber vulcanizates, there is no significant difference in the values obtained from physical and chemical data. However, Morris[12], using the same accelerator in natural rubber stocks, obtained only a slight difference in the values from the two sources. It is worth noting, however, that here, as in all the reported work with natural rubber, the values obtained from chemical data were somewhat larger than those obtained from physical data, even though the differences were slight.

The constancy of the values obtained over a fivefold variation in sulfur content and with a corresponding variation in sulfur-accelerator ratio is also a striking result. It is remarkable that the values obtained were in such close agreement with the arbitrary value obtained from the Government memorandum[5].

ACKNOWLEDGMENT

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REFERENCES

[1] Bourne, *India Rubber World* **33**, 93 (1905); Spence and Young, *Z. Chem. Ind. Kolloide* **11**, 28 (1912); Bourne, *India-Rubber J.* **45**, 120 (1913); Cranor, *India Rubber World* **61**, 137 (1919); Twiss and Brazier, *J. Soc. Chem. Ind.* **39**, 125T (1920); Sheppard and Krall, *Ind. Eng. Chem.* **14**, 951 (1922); Sheppard, *India Rubber World* **80**, 56 (1929); Park, *Ind. Eng. Chem.* **22**, 1004 (1930); Sandstrom, *Ind. Eng. Chem.* **25**, 684 (1933); Eliel, *Trans. Inst. Rubber Ind.* **12**, 161 (1936); Gerke, *Ind. Eng. Chem.* **31**, 1478 (1939).

[2] Williams, in "Chemistry and Technology of Rubber", Edited by Davis and Blake, Am. Chem. Soc. Monograph, No. 74, Reinhold Publishing Corp., **1937**, Chap. VI; Fisher, *Ind. Eng. Chem.* **31**, 1381 (1939); Gerke, *Ind. Eng. Chem.* **31**, 1478 (1939).

[3] Morris, *Ind. Eng. Chem.* **25**, 1400 (1933); Street and Ebert, RUBBER CHEM. TECH. **14**, 211 (1941); Sebrell and Dinsmore, *India Rubber World* **103**, No. 6, 37 (1941); **104**, No. 1, 45 (1941); Anonymous, *India Rubber World* **106**, 458, 575 (1941); **107**, 37 (1942); Carlton and Reinbold, *Rubber Age* (N. Y.) **52**, 29 (1942); Drogin, *Rubber Age* (N. Y.) **51**, 483 (1942); Garvey and Freeze, *Ind. Eng. Chem.* **34**, 1277 (1942); Street, in "Vanderbilt Handbook", **1942**, p. 65; Vila, *Ind. Eng. Chem.* **34**, 1269 (1942); Brackley, *Rubber Age* (N. Y.) **54**, 331 (1943); Cheyney and Robinson, *Ind. Eng. Chem.* **35**, 976 (1943); Jones and Snyder, *India Rubber World* **108**, 137 (1943); Neal, *Rubber Age* (N. Y.) **53**, 31 (1943); Sebrell, *Ind. Eng. Chem.* **35**, 736 (1943); Morris, Milton, Montermoso and Werkenthin, *Ind. Eng. Chem.* **35**, 646 (1943); Morris, James and Werkenthin, *Ind. Eng. Chem.* **35**, 864 (1943).

[4] Street and Dillon, *J. Applied Physics* **12**, 45 (1941); Drogin, *Rubber Age* (N. Y.) **51**, 483 (1942); Street, in "Vanderbilt Handbook", **1942**, p. 65; Cheyney and Robinson, *Ind. Eng. Chem.* **35**, 976 (1943); Morris, Mitton, Montermoso and Werkenthin, *Ind. Eng. Chem.* **35**, 646 (1943).

[5] Simmons, *India Rubber World* **107**, 497 (1943); *Rubber Age* (N. Y.) **52**, 305 (1943).

[6] Vila, *Ind. Eng. Chem.* **34**, 1269 (1942).

[7] Am. Soc. Testing Materials, "Standards on Rubber Products", Designation D15–41 (1941); Designation D412–41 (1941).

[8] Cheyney, *Ind. Eng. Chem. Anal. Ed.* **15**, 164, (1943).

[9] Oldham, Baker and Craytor, *Ind. Eng. Chem. Anal. Ed.* **8**, 41 (1936).

[10] Cheyney and Robinson, *Ind. Eng. Chem.* **35**, 976 (1943).

[11] Gerke, *Ind. Eng. Chem.* **31**, 1478 (1939).

[12] Morris, *Ind. Eng. Chem.* **25**, 1400 (1933).

EFFECT OF LOW TEMPERATURES ON YOUNG'S MODULUS OF ELASTOMERS *

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The literature reveals a considerable diversity in test methods employed to determine the effects of low temperatures on the physical properties of rubber compounds. With few exceptions these tests consist principally in extending measurements of the same properties used by the practical rubber technologist, and normally measured at room temperatures, to the desired low-temperature range.

Somerville[1], for example, reported tensile strength, modulus at 500% elongation, elongation at break, T-50 data, and hardness (durometer) of two vulcanized pure-gum compounds at temperatures as low as −60° C. The difficulties encountered in attempting to use measurements of some of these properties as a serviceability index are best illustrated by Somerville's observation that compounds at −60° C, which were so brittle they shattered by a light hammer blow, showed 500% elongation when tested on the regular Scott tensile machine. LeBlanc and Kröger[2] described elongation and permanent set tests on rubber compounds as low as −61° C. These results were then applied to a theory of vulcanization. Gibbons, Gerke, and Tingey[3] developed the well known T-50 test, employing the temperature at which a stretched, cold-hardened sample of rubber softens sufficiently to lose 50% of its elongation when frozen as a measure of state of cure (amount of combined sulfur). Gibbons, Gerke, and Cuthertson[4] elaborated on this low-temperature test as an analytical method for determining state of vulcanization[5]. Sagajllo, Bobinska, and Saganowski[6] reported that susceptibility to freezing increases with elongation, especially for elongations above 200%. Permanent set was employed as a serviceability index in this work, and it was concluded that aircraft shock absorber thread showed no seroius loss in elastic properties down to −20° C. Tener, Kingsbury, and Holt[7] conducted tensile and modulus tests over a wide range (−70° to +147° C) on ring-type samples and the usual Scott-type tensile tester. They concluded that differences in freezing characteristics of stocks attributable to compounding changes were differences in degree rather than kind. They also pointed out that the effects of low temperature were smaller on low moduli than on high moduli. Harrington[8] reported results of tests conducted at temperatures down to −10° C. Permanent set was employed as a freezing index in these tests.

One attempt to determine low-temperature serviceability of rubber by measurements made directly on the finished article (rather than on the material itself) was reported by McCortney and Hendrick[9]. Selker, Winspear, and Kemp[10] described a simple apparatus for determining brittle point, or the temperature below which vulcanizates become nonserviceable. The dependence of their measured brittle-point temperature on test conditions, particularly

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rate of application of stress, was demonstrated by Kemp, Malm, and Winspear[11] and by Morris, James, and Werkenthin[12]. An autographic modification of the T-50 test and a hardness index based on durometer readings were reported by Yerzley and Fraser[13] in work on the effects of low temperature on neoprene vulcanizates. Garvey, Juve, and Sauser[14] reported results on Hycar OR; they listed as low-temperature indices (1) the temperature at which the sample failed to recover spontaneously (rapidly), (2) the temperature at which the sample failed to bend under a "light" load, (3) the temperature at which the sample failed to bend under a "heavy" load, and (4) brittleness temperature. No details were given. A simple low-temperature flexing apparatus was reported by Martin[15] and later tentatively adopted by the A.S.T.M. Douglas[16] described some tests on dead-load compression at low temperatures. In a rather broad sense, the above described tests do not measure a fundamental property of the material except insofar as this property can be expressed in terms of the particular apparatus and test techniques employed.

Stifler and Mitchell[17] published briefly on the development of a method for measuring coefficient of rigidity and Young's modulus at temperatures as low as −30° C. Koch[18] later described in detail a method for determining Young's modulus in supports are accurately machined in the form of a saddle; the dimensions of the support and of loading foot *H* are shown in bending. This test is one of the few in the literature in which a basic physical property of the material under test is measured. Largely because of this feature, the principles of Koch's test were adopted as the basis for the low-temperature test described here. Since this work was initiated, Kish[19] has published results on a similar bending test. A modified beam-bending test was described by Werkenthin[20]. A tensiometer stiffness test was developed by Green, Cholar, and Wilson[21], in which Young's modulus and a stiffening temperature are determined from simple beam-bending observations. Gehman's work[22] also falls in this class of test, inasmuch as his results indicate the dependence of dynamic stiffness and dynamic resilience on temperature.

Publications by Wood, Bekkedahl, Roth, Peters, and Matheson[23] and by Ruhemann and Simon[24] on crystallization, melting, density, etc., have aided in establishing sound techniques and in interpreting experimental results.

THEORETICAL CONSIDERATIONS

Regardless of the low-temperature test employed, one of the first steps in establishing a satisfactory technique is the specification of time of exposure of the sample to the desired low temperature before testing. There has apparently been considerable confusion in this respect, since conditioning times in the tests described above vary from unspecified to between 5 minutes and 5 hours, irrespective of material or possible service conditions. Investigators at the National Bureau of Standards have demonstrated that, for natural rubber and some of the synthetic elastomers, two distinct changes take place on lowering the temperature—true crystallization and a second-order transition in which no change in volume is involved. Changes in physical characteristics resulting from second-order transition changes do not depend critically on time. Such changes in properties take place quickly and at a definite temperature. On the other hand, changes in properties resulting from crystallization may take hours, days, weeks, or longer, depending on the particular temperature employed. The temperature at which natural rubber crystallizes most rapidly is about −20° C; for Neoprene-GN it is reported to be about 0° C. Above

and below these temperatures crystallization proceeds at a slower rate. All rubberlike materials exhibit second-order transition, but only a relatively small number of materials exhibit crystallization (for example, unvulcanized rubber, Thiokol-A, Neoprene-GN). Specification of an arbitrary conditioning time of 5 hours, for example, regardless of type of material, is unnecessary and, in the case of comparisons between different types of materials, misleading. Likewise, any attempt to compare materials (which exhibit changes in properties resulting from crystallization) on the basis of exposure at a given temperature for a specified time is almost certain to be misleading. The specified temperature may be near the optimum rate of crystallization temperature of one of the materials and many degrees above or below the optimum of another. Since physical changes resulting from a second-order transition take place rapidly, a conditioning time of 5 to 10 minutes, plus the time required to ensure uniformity of temperature throughout the body of the sample, should be adequate for those materials which do not undergo crystallization.

In view of these observations, it was decided to limit this work to the observation of changes resulting from the second-order transition. All tests were thus conducted as quickly as was consistent with equilibrium temperature conditions, and frequent checks were made to detect any progressive stiffening which might have resulted from the onset of crystallization.

The deflection method of Koch has been criticized[11] because it fails to predict how a given material will respond to severe deformation in service; it is admitted, however, that considerable information as to the progress of stiffening above the brittle point can be obtained from such data.

The brittleness technique can similarly be criticized on the grounds that it fails to predict how rapidly a given material will stiffen or harden. Although this technique determines the temperature below which a material is nonserviceable, it will be shown that a real difference in serviceability may exist between compounds having the same brittle point.

Thus it appears that neither bending nor brittleness techniques alone are sufficient for a complete serviceability analysis. A combination of the two, however, does give all the pertinent information required by the rubber technologist in compounding a given material for a particular application. The method of Koch in bending and that of Selker, Winspear, and Kemp in brittleness were adapted in this investigation to furnish the required data.

APPARATUS AND TEST TECHNIQUES

Young's modulus data were calculated from experimental bending observations made on the apparatus shown in Figure 1.

Thirty sample supports, *A*, are arranged around the circumference of a heavy turntable, *B*, which is 19 inches (48.2 cm.) in diameter and 0.625 inch 1.59 cm.) thick. These sample supports are accurately spaced and located with respect to a set of thirty No. 5 taper holes, *C*, in the edge of turntable *B*. A Bakelite rod, *D*, slides in a Bakelite bushing, *E*, which is mounted rigidly to and extends through the wall of refrigerated box *F*. By manipulating rod *D* from the outside of the box, it is possible to engage any one of holes *C* by a tapered pin, *G*. Whenever the pin is thus engaged in one of the holes, one of the sample supports *A* is automatically located accurately underneath a loading foot, *H*, which has the same contour as the sample supports. A shaft, *I*, extends through a second Bakelite sleeve, *J*. This shaft rotates turntable *B* through a set of bevel gears underneath the turntable and is driven (through a

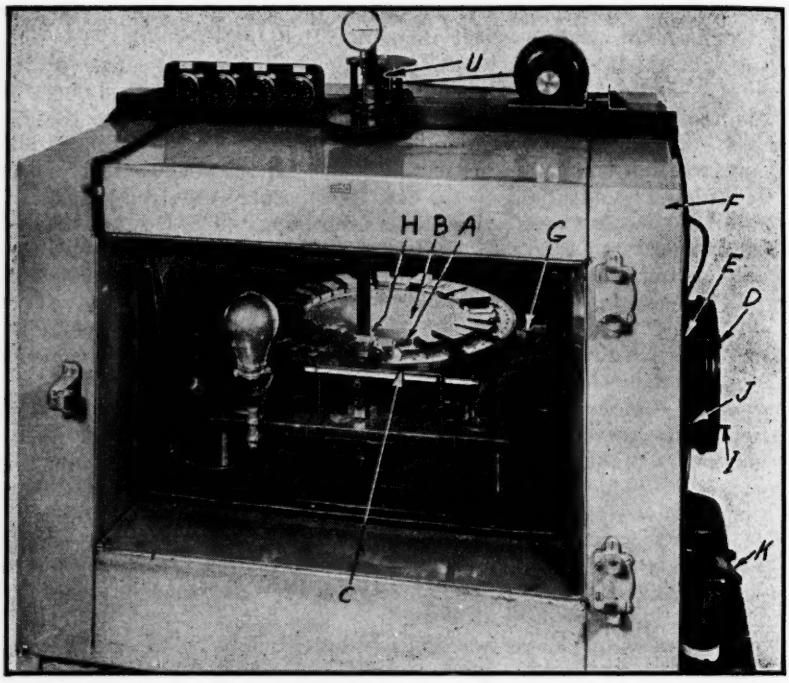

FIG. 1.—Apparatus for measuring Young's modulus.

friction clutch), by a small motor, *K*, located outside of the refrigerated box. The sample supports are accurately machined in the form of a saddle; the dimensions of the support and of loading foot *H* are shown in Figure 2. A Bakelite sleeve or guide housing, *L*, extends through the top of the refrigerated box and is rigidly held by two nuts, *M*. A second piece of Bakelite tubing, *N*, slides through the guide housing. A handwheel, *O*, threaded to fit tubing *N*, enables this piece to be raised or lowered at will. A weight pan, *P*, is attached to the upper end of *N*, and loading foot *H* is fixed to it at the lower end. A small Bakelite rod, *Q*, extends through *N*, terminating at loading foot *H* at one end and at the foot of a dial gauge, *R*, at the other. The only load carried by *Q* is the dead-load reaction of the dial gauge.

In practice, the loading foot, loading weights *S*, and dial gauge rod are raised by means of the handwheel, so that the loading foot does not touch samples *T* as they rotate with the turntable. The latter is rotated continuously during a test (except during the time observations on a given sample are being made) to ensure uniform temperature distribution in all samples. An air mixing fan, *U* (Figure 1), driven from the outside of the box, also aids in providing uniform air temperature through the test chamber.

The test samples in the form of blocks 1 inch wide, 2.25 inches long, and 0.10–0.40 inch thick (2.54 × 5.72 × 0.254–1.02 cm.) are placed over the sample supports (the loading foot assembly being raised clear of all samples), the refrigerator door is closed, and the air-circulating fan and turntable rotating motor are turned on. The refrigerator motor is then started, and the thermo-

stat is set at 0° C. Experiments indicated that the temperature of the interior of the thickest sample blocks employed lagged behind the air temperature by about 10 minutes. An additional 10-minute conditioning is given the samples to ensure adequate temperature uniformity, for the observation of modulus changes resulting from a second-order transition. Bending deflection *vs.* load observations are thus begun 20 minutes after the refrigerator air has reached a given temperature. Each sample, in turn, is brought under the loading foot,

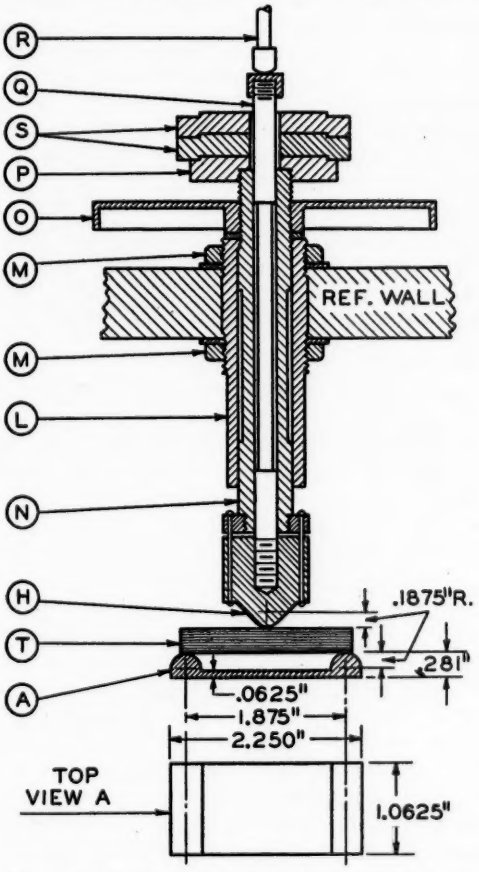

FIG. 2.—Details of loading foot, sample, and sample support.

and the handwheel is rotated so that the minimum dead load of 368 grams (0.81 pound) is applied to the center of the sample. An additional load, W, is then placed on the weight pan. The total load (dead load plus W) is impressed on the sample for 5 seconds, following which W is removed. When the dial gauge reading ceases to change (2–3 seconds), indicating equilibrium, the reading is recorded as R_0. Weight W is then reapplied and allowed to remain for 10 seconds. At the end of this time the dial gauge will have again come to rest in the majority of cases, and the reading is recorded as R_1. The difference $R_1 - R_0$ is taken to be the bending deflection produced by load W. A

few additional precautions are necessary in some instances, particularly in the case of measurements on very soft, "logy" samples at relatively high temperatures. In the first place, load W must be preselected in advance to give a deflection $(R_1 - R_0)$ less than 0.025 inch (0.635 mm.).

If highly accurate absolute values are desired, the deflection $(R_1 - R_0)$ should be corrected by subtracting the contraction of the loading rod and also the distance the sample supports and presser foot have "penetrated" into the sample. This can be determined in the following manner: A solid block of material (steel or Bakelite), at least 0.25 inch thick, 1.5 inches long, and 1 inch wide (0.635 × 3.81 × 2.54 cm.) is placed under a second sample of the same stock, with the same thickness and width. The procedure outlined above is followed. The measured deflection, $R_1' - R_0'$, is the sum of the amount the presser foot has penetrated into the sample plus the amount the loading rod has contracted or bent laterally under load W. The latter is determined independently by measuring the deflection produced by a given load with the presser foot resting directly on a steel block. This small correction, Δ, need be determined only once for a given load and loading rod, since it is independent of any sample. The amount of penetration of the sample supports is then calculated by subtracting Δ from $R_1' - R_0'$ and dividing by 2 (since there are two supports sustaining the loaded sample). The final corrected deflection is thus given by:

$$d = (R_1 - R_0) - (R_1' - R_0') - \tfrac{1}{2}[(R_1' - R_0') - \Delta] \qquad (1)$$

After the above procedure has been followed for all the samples under test, the presser foot is raised clear of the samples and the turntable is again allowed to rotate continuously. The thermostat is then set to −20° C, and the process is repeated. The entire procedure is repeated at −40° and −60° C (temperatures decreasing) and at 5° C intervals back to 0° (temperatures increasing). A double set of readings is thus obtained at −40°, −20°, and 0° C. If a physical change resulting from crystallization is contributing to the bending modulus, the readings at these three temperatures (temperatures increasing) do not agree with the observations made as the temperatures were lowered. Unless specifically noted to the contrary, all the data presented were obtained under such conditions that no significant crystallization effects could be detected. It should be remembered, however, that in the case of some of the materials, *e.g.*, Neoprene-GN stocks, a crystallization effect would have been obtained had the test been continued long enough. No attempt has been made in this work to separate the two phenomena, other than to make the total cold-conditioning time so short that crystallization (where it occurred) was not appreciable. Because of the difficulties of obtaining temperatures as low as −60° C in a short time and because of the time required to make direct bending measurements plus the necessary corrections, it is sometimes impossible to finish an entire run in one day. Whenever this happens, the thermostat is set to the temperature at which the last series of readings was made, and another series is obtained at the same temperature at the beginning of the following day. Agreement between the two series of data is always obtained unless crystallization has taken place. Disagreement indicating appreciable crystallization during a test run has been observed only in a few instances, *e.g.*, natural rubber in a very low state of cure and Neoprene-GN during a special long-time experiment.

Young's modulus can be calculated from the above data by means of the well known beam-bending formula:

$$E = Wl^3/4dbh^3 \qquad (2)$$

where E = Young's modulus
W = load producing a deflection, d
d = deflection (corrected) produced by load W
l = distance between center lines of sample supports
b = width of sample
h = thickness of sample

The data are presented in the form of graphs showing the change in Young's modulus as a function of temperature. No significance is to be attached to the logarithmic modulus scale employed. It was adopted merely to enable the entire range of moduli to be shown on the same curve and yet employ a reasonably sensitive scale in the low modulus range.

Brittleness data were obtained on an apparatus similar to that described by Selker, Winspear, and Kemp[10]. No attempt was made in the present work to study the effect of rate of deformation on brittle point. All results were obtained by turning the crank manually as rapidly as possible. The apparatus is shown in Figure 3.

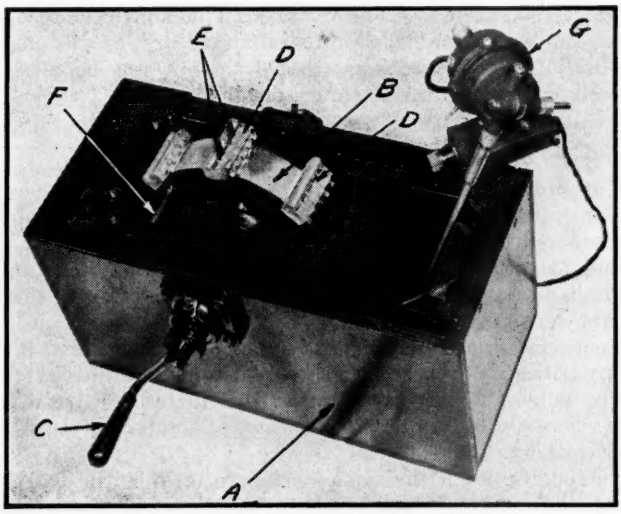

FIG. 3.—Apparatus for measuring brittleness temperature.

It consists of a well-insulated tank A, 5.5 × 18 × 9 inches (14.0 × 45.7 × 22.9 cm.), a segment of a wheel B with a radius of 6 inches (15.2 cm.), a crank C, clamps D for holding samples E, and a striker bar F which can be adjusted to provide any desired clearance between the outer or striking surface of sample E and bar F. A stirrer motor, G, agitates the liquid medium and thus provides a uniform temperature throughout. Temperatures are measured by a thermometer (not shown) located near the striker bar. Provisions were originally made to test fifteen samples at a time (five in each of the three sets

of clamps shown), but it was found that the rate of deformation was sensibly affected by successive impacts. Hence the final technique was based on testing samples only in the center set of test clamps. Clearance between striker bar and striking surface of the samples seemed to affect the results somewhat, and after some experimentation a standard clearance of 0.050 inch (0.127 cm.) was adopted. (Total clearance between top-most part of circle and striker bar is actually set at 0.127 cm. plus the normal thickness of the samples to be tested.) The samples employed are 0.5 inch wide, 1.5 inches long, and 0.05–0.1 inch thick (1.27 × 3.81 × 0.127–0.254 cm.). If nothing is known of the stock to be tested, the bath temperature is lowered to and held at 0° C while the samples are placed in the clamps. The segment is then turned so samples are immersed. A conditioning period of 10 minutes has been adopted, although bath temperatures are attained at the center of the sample in about 2 minutes. The crank is then given a rapid, firm turn, after which the samples are examined for breaks or cracks. If none of the samples is found to be broken, a fresh set of samples is inserted in the clamp, the bath temperature is lowered 5° C, and the process is repeated. Each sample is cold-flexed only once, whether or not it breaks. This process is repeated until all samples have broken at some temperature. By repeating the above process in 1° intervals within the 5° range thus established, a brittle point accurate to 1° C can easily be obtained. The brittle points recorded in the present work are the highest temperatures at which the sample in question actually broke. In all cases the sample failed to break when the test temperature was raised 1° C above the recorded brittle point. As in similar work of this kind, granulated dry ice was employed as a coolant. The liquid employed was ethanol since it was believed to have a negligible swelling effect on the elastomers tested.

RESULTS

The variation in Young's modulus with temperature change is shown in Figure 4*A* for optimum cures of gum stocks of natural rubber, polybutadiene, polymers composed of 85 parts butadiene and 15 parts styrene, of 75 parts butadiene and 25 parts styrene (GR-S), and 60 parts butadiene and 40 parts styrene. Similar data for typical tread-type stocks containing the same base elastomers are shown in Figure 4*B*.

The styrene content of a butadiene-styrene polymer affects its low-temperature modulus critically. The relatively small temperature effect in the case of the polybutadiene stocks should make this material extremely useful in applications where flexibility over a wide range of low temperatures is the chief factor under consideration.

Brittle temperatures for the same stocks are recorded in Tables I and II, together with the formulas. Although the brittle-point temperatures of the 75 butadiene–25 styrene polymer stocks are actually lower than those of the natural rubber stocks, the moduli of the latter are considerably lower than those of the former over most of the entire range studied. On the basis of brittleness data alone, this 75–25 polymer would be considered appreciably more cold resistant than natural rubber. The modulus data indicate definitely, however, that this butadiene-styrene polymer would stiffen and thus become nonserviceable at higher temperatures than would natural rubber.

Under the test conditions which prevailed in the experiments, the measured deflections at very high moduli are small and thus subject to considerably larger errors than those at the higher temperatures. The curves for moduli

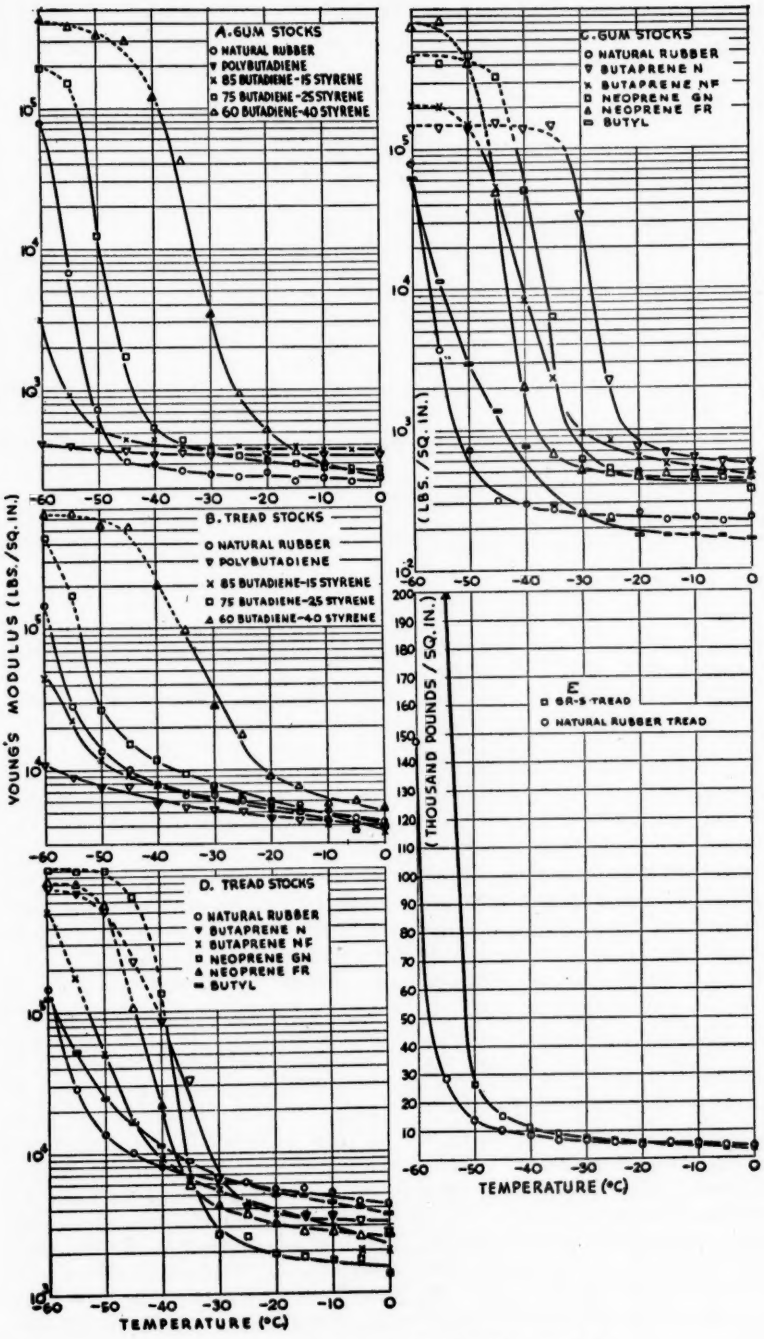

FIG. 4.—Young's modulus as a function of temperature.

TABLE I

GUM STOCK FORMULAS FOR NATURAL RUBBER AND BUTADIENE POLYMERS

Stock	*A*	*B*	*C*	*D*	*E*
Sulfur	3.0	2.0	2.0	2.0	2.0
Zinc oxide	3.0	5.0	5.0	5.0	5.0
Stearic acid	0.5	0.5	0.5	0.5	0.5
Captax accelerator	1.0	1.5	1.5	1.5	1.5
Agerite-Neozone-D	1.0	...	...	...	...
Natural rubber	100.0	...	...	...	...
Polymerized polybutadiene	...	100.0	...	...	...
Butadiene-styrene polymers					
85–15	...	...	100.0	...	...
75–25	...	...	...	100.0	...
60–40	...	...	...	...	100.0
Cure at 270° F (min.)	75	100	100	100	100
Brittle temperature (° C)	−53	<−72	−65	−63	−46

TABLE II

TREAD STOCK FORMULAS FOR NATURAL RUBBER AND BUTADIENE POLYMERS

Stock	A_1	B_1	C_1	D_1	E_1
Sulfur	3.0	2.0	2.0	2.0	2.0
Zinc oxide	3.0	5.0	5.0	5.0	5.0
Stearic acid	3.5	3.0	3.0	3.0	3.0
Captax accelerator	1.0	1.5	1.5	1.5	1.5
Agerite–Neozone-D	1.0	...	...	...	...
Pine tar	3.0	...	...	...	...
Bardol	...	5.0	5.0	5.0	5.0
Channel black	50.0	50.0	50.0	50.0	50.0
Natural rubber	100.0	...	...	...	...
Polymerized polybutadiene	...	100.0	...	...	...
Butadiene-styrene polymers					
85–15	...	...	100.0	...	...
75–25	...	...	...	100.0	...
60–40	...	...	...	...	100.0
Cure at 270° F (min.)	75	100	100	100	100
Brittle temperature (° C)	−53	<−72	−65	−63	−42

exceeding 10^5 pounds per square inch (6.9×10^9 dynes per sq. cm.) are dotted (Figure 4) to indicate that the absolute values may be in error by as much as 20 per cent. This is not a serious defect in the method, however, since stocks having considerably lower moduli are required for normal service.

The curves, in general, indicate that Young's modulus increases slowly at first as the temperature is lowered. For each elastomer a temperature exists below which the modulus begins to rise much more rapidly. The temperature at which this rather sudden rise occurs has been used[21] as a convenient qualitative freezing index, but otherwise its physical significance is not clear. Since the rate of increase of modulus with decrease in temperature is not the same for all elastomers, this "stiffening temperature" cannot be determined with a uniform degree of accuracy. The data for the natural rubber and the GR-S tread stocks taken from Figure 4*B* were replotted (Figure 4*E*) on a linear scale to illustrate the form of the curves in the region of this stiffening temperature.

The variation in Young's modulus with temperature change for optimum cures of Butaprene-N, Butaprene-NF, Neoprene-GN, Neoprene-FR, and Butyl (GR-I) gum stocks are shown in Figure 4*C*. The data for the natural rubber um stock of Figure 4*A* are repeated to provide a common basis for comparison. milar data for optimum cures of tread type compounds having the same base

elastomers are shown in Figure 4*D*. Stock formulas and brittle-point temperatures are given in Table III.

In the case of the Butyl stocks, the modulus does not change rapidly in a relatively small temperature region; hence a "stiffening temperature" would be difficult to define.

TABLE III

FORMULAS FOR BUTAPRENE, NEOPRENE, AND BUTYL STOCKS

	Gum stock formulas					Tread stock formulas				
	F	G	H	I	J	F_1	G_1	H_1	I_1	J_1
Sulfur	2.5	2.5	...	1.0	2.0	3.0	3.0	...	1.0	2.0
Zinc oxide	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Stearic acid	1.0	1.0	0.5	2.0	1.5	3.0	3.0	0.5	2.0	3.0
Magnesia	...	...	4.0	4.0	...	...	...	4.0	4.0	...
Agerite-Neozone-D	...	...	1.0	1.0	...	...	...	1.0	1.0	...
Light mineral oil	...	...	...	2.0	...	...	...	...	2.0	...
Cottonseed oil	...	...	2.5	...	...	...	...	2.5	...	...
Bardol	...	...	...	2.0	...	...	...	...	2.0	...
Dibutyl phthalate	...	...	...	...	...	20.0	20.0	...	...	...
Captax	1.5	1.5	...	...	0.5	1.5	1.5	...	...	0.5
Altax	...	...	0.75	...	...	...	...	0.75	...	...
Pip-Pip	...	...	0.50	...	...	...	...	0.50	...	...
Tuads	...	...	...	...	1.0	...	...	...	...	1.0
Channel black	...	...	...	...	...	50.0	50.0	36.0	39.0	50.0
Butaprene-N	100.0	...	...	...	...	100.0	...	...	...	...
Butaprene-NF	...	100.0	...	...	...	...	100.0	...	...	...
Neoprene-GN	...	...	100.0	...	...	...	...	100.0	...	...
Neoprene-FR	...	...	...	100.0	...	...	...	...	100.0	...
Butyl (GR-I)	...	...	...	...	100.0	...	...	...	...	100.0
Cure minutes										
270° F	75	100	100	...	...	75	100	100	...	...
280° F	...	...	...	60	...	...	...	...	60	...
300° F	...	...	...	...	75	...	...	...	...	100
Brittle temperature (° C)	−41	−62	−37	−44	−48	−43	−60	−39	−46	−39

Both Butaprene-NF and Neoprene-FR polymers were introduced in response to the need for Butaprene-N and Neoprene types having better "freeze resistance" than the latter basic polymers. The data indicate that both the modulus at low temperatures and the brittle-point temperatures have been appreciably lowered by these polymer changes, the improvement being somewhat larger in the case of the Butaprene type.

Although different stock formulations were employed by Selker, Winspear, and Kemp[16], the brittle temperatures of similar stocks having the same base polymer were found to agree closely with those shown in Tables I to IV. In

TABLE IV

BRITTLE-POINT TEMPERATURE AS A FUNCTION OF CURE

Natural rubber			GR-S		
Cure at 270° F. (min.)	Brittle temp. (° C)		Cure at 270° F. (min.)	Brittle temp. (° C)	
	Gum	Tread		Gum	Tread
10	−56	....	10	−65	−60
40	−53	−53	60	−66	−62
80	−53	−53	110	−63	−63
130	−52	−53	160	−64	−62
190	−52	−52	210	−63	−62

general, moduli of both gum- and tread-type stocks change slope in a comparatively narrow temperature range. These observations suggest that both Young's modulus and brittle temperatures as measured are fundamental properties of the base polymer, and are thus relatively unaffected by reinforcing materials, antioxidants, or inert fillers. The proportions of combined sulfur

and relatively large proportions of oils and other softeners, however, significantly affect both properties.

The effect of state of cure on Young's modulus at low temperatures is shown for the natural rubber and GR-S tread-type stocks in Figure 5. Although a complete range of cures of the GR-S tread-type stocks was investigated, it was not found possible to measure the uncured and low-cure natural rubber tread stock in this manner because of the time-stiffening effect. A measurable

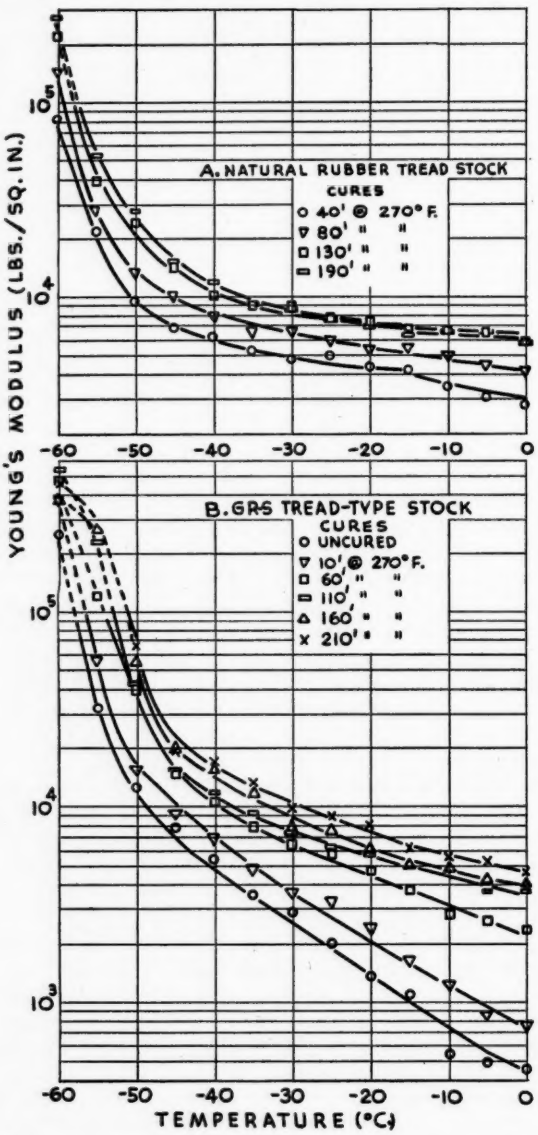

FIG. 5.—Effect of cure on Young's modulus at low temperatures.

change in Young's modulus was observable in as little as 24 hours in the case of the uncured, natural rubber tread-type stock, an indication that significant crystallization had taken place.

Brittle-point temperatures at various cures are shown in Table IV. Brittle temperatures in these instances do not depend critically on state of cure.

The rate of change of modulus with time at 0° C is shown, for the Neoprene-GN stocks, in Figure 6. These data illustrate another type of test which can be run on the apparatus described, and also indicate the length of time required in studying the effects of crystallization on low-temperature phenomena.

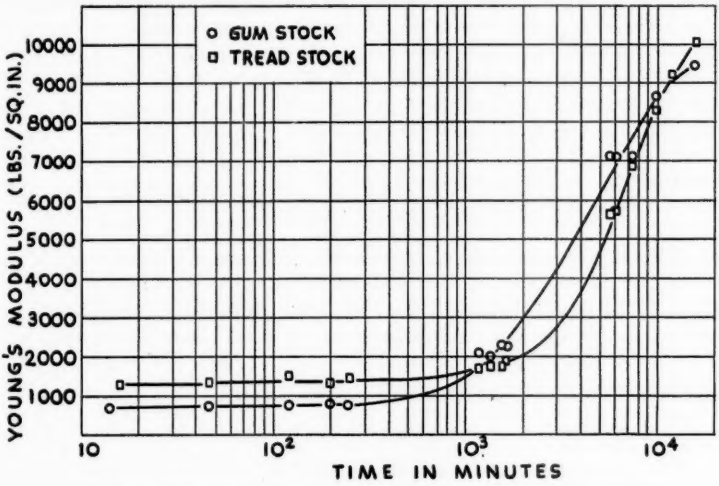

FIG. 6.—Effect of freezing time on Young's modulus of Neoprene stocks.

A preliminary study of the effect of time of conditioning at low temperatures on brittle-point temperatures confirmed the statement that crystallization stiffens and hardens a stock but does not necessarily add to its brittleness. In this study the brittle temperatures of three commercial compounds having Neoprene-GN bases were determined in the usual manner. The brittle temperatures were found to be −37°, −34°, and −38° C. Additional test samples of these three stocks were then stored in a test-tube in an ice chest for 32 days. At intervals samples were removed from the test-tubes, quickly inserted in the birttleness tester clamps, and tested in the regular manner, with the bath set at −32° C. In no case, even after 32 days, did any of the samples break at the latter temperature, although a progressive increase in stiffness was observed when the cold-aged samples were being inserted in the clamps. The test was terminated when the samples were accidentally removed from the ice chest before an absolute brittle temperature could be obtained. It is planned to repeat both bending modulus and brittle-point measurements on cold aging of the same Neoprene-GN stock.

CONCLUSIONS

The data presented should be of value to the rubber technologist who may be called on to produce a compound having a given base polymer capable of performing satisfactorily down to a specified low temperature. Although

natural rubber is basically more cold-resistant than some of the other synthetic elastomers, it has been found possible to add larger quantities of softeners and modifiers to the latter (without causing too serious a decrease in mechanical properties) than can be added to natural rubber. Consequently, it is possible to compound synthetic elastomer stocks having better low-temperature properties than natural rubber stocks.

In the case of material which does not exhibit crystallization, it should be possible (either from experience or by a simple test at normal temperatures) to set an upper limit for the Young's modulus of the proposed stock consistent with satisfactory operation. A modulus *vs.* temperature curve of the stock would then indicate definitely whether the observed modulus at the specified low temperature exceeded the limit previously set. If it did not and, in addition, the brittle-point temperature was found to be below the specified operating temperature, successful operation could reasonably be expected.

In general, it is not necessary to calculate Young's modulus in all cases. For a given load and sample size, the deflection as measured would serve equally well as an index.

ACKNOWLEDGMENT

The writer wishes to express his thanks to J. H. Dillon for many helpful discussions during the course of this work, and to J. N. Street and The Firestone Tire and Rubber Company for permission to publish this paper. It is a pleasure to acknowledge the assistance of Floyd S. Conant in performing a large part of the testing reported in this paper, and of Frank S. Grover and J. Koch in the mechanical design and construction of the apparatus.

REFERENCES

[1] Somerville, *Proc. Rubber Tech. Conf. London*, **1938**, p. 773.
[2] Le Blanc and Kröger, *Kolloid-Z.* **37**, 205 (1925).
[3] Gibbons, Gerke and Tingey, *Ind. Eng. Chem. Anal. Ed.* **5**, 279 (1933).
[4] Gibbons, Gerke and Cuthbertson, *Proc. Rubber Tech. Conf. London*, **1938**, p. 861.
[5] Am. Soc. Testing Materials, Specification D599–40T, D-11 Comm. Report; Standards, **1940** supplement, Part III, p. 341.
[6] Sagajllo, Bobinska and Saganowski, *Proc. Rubber Tech. Conf. London*, **1938**, p. 749.
[7] Tener, Kingsbury and Holt, Bur. Standards, Sci. Tech. Paper No. **364**, 1928, p. 22.
[8] Harrington, *Proc. Rubber Tech. Conf. London*, **1938**, p. 787.
[9] McCortney and Hendrick, *Ind. Eng. Chem.* **33**, 579 (1941).
[10] Selker, Winspear and Kemp, *Ind. Eng. Chem.* **34**, 157 (1942).
[11] Kemp, Malm and Winspear, *Ind. Eng. Chem.* **35**, 488 (1943).
[12] Morris, James and Werkenthin, *Ind. Eng. Chem.* **35**, 864 (1943).
[13] Yerzley and Fraser, *Ind. Eng. Chem.* **34**, 332 (1942).
[14] Garvey, Juve and Sauser, *Ind. Eng. Chem.* **33**, 602 (1941).
[15] Martin, *Rubber Age* (N. Y.) **52**, 227 (1942).
[16] Douglas, *India-Rubber J.* **80**, 899 (1930).
[17] Stifler and Mitchell, *Phys. Rev.* **37**, 1683 (1931).
[18] Koch, *Kunststoffe* **28** (1928); RUBBER CHEM. TECH. **14**, 799 (1941).
[19] Kish, *Rubber Age* (N. Y.) **53**, 139 (1943); *Oil Gas J.* **42**, 43 (1943).
[20] Werkenthin, Report to Tech. Comm., Mech. Division, Am. Soc. Testing Materials, May 6, **1943.**
[21] Green, Cholar and Wilson, *Rubber Age* (N. Y.) **53**, 319 (1943).
[22] Gehman, *J. Applied Physics* **13**, 402 (1942).
[23] Bekkedahl, *J. Research Natl. Bur. Standards* **13**, 411 (1934); Bekkedahl and Matheson, *J. Research Natl. Bur. Standards* **15**, 503 (1935); Bekkedahl and Wood, *Ind. Eng. Chem.* **33**, 381 (1941); *J. Chem. Physics* **9**, 193 (1941); Wood, Bekkedahl and Peters, *J. Research Natl. Bur. Standards* **23**, 571 (1939); Wood, *J. Chem. Physics* **10**, 403 (1942); Wood, Bekkedahl and Roth, *J. Research Natl. Bur. Standards* **29**, 391 (1942).
[24] Ruhemann and Simon, *Z. physik. Chem.* **138A**, 1 (1928).

RESILIENT ENERGY

E. C. B. Bott

The Anchor Chemical Co., Ltd., Clayton, Manchester, England

Rubber Chemistry and Technology, Volume 16, No. 3, pages 591–608, July 1943, contains an article entitled "Resilient Energy", by E. C. B. Bott.

The author has called our attention to three errors which appear in the original article in the *Transactions of the Institution of the Rubber Industry*, Volume 18, No. 4, pages 147–165, December 1942, and which were consequently transcribed into the reprinted version in Rubber Chemistry and Technology.

The errors and corrections are itemized below, and in all cases the pages given refer to the pages in Rubber Chemistry and Technology.

Page 598.—Before the fourth, fifth and sixth terms on the right-hand side of Equation (13), insert a plus (+) sign.

Page 599.—Before the third term on the right-hand side of Equation (13a), insert a plus (+) sign.

In line 9, delete the number "2" at the end of the line. The complete line should read: "*Function* 1. Tensile strength = T (E + 1), taken from the table of differences on page 597."

Page 600.—In line 9, delete the superscript "2" which follows the expression: "under 5.70 per cent/5′ ", at the end of the line.

THE EFFECTS OF MILLING ON THE SOFTNESS OF RUBBER

I. TEMPERATURE AND FRICTION *

A. Haehl and Jean le Bras

Although the process of softening rubber by mastication has been the subject of repeated investigation, the literature contains no references to systematic experiments in this field. It is with a view to making up for this lack of information that the work described in the present paper was undertaken.

A survey of the literature shows several papers of interest in connection with the work to be described in the present paper, particularly the papers of Grundy and Schidrowitz[1], Griffiths[2], The Goodyear Tire and Rubber Company[3], Shoaff[4], Bachmann, Behre and Blankenstein[5], and Busse and Cunningham[6].

Grundy and Schidrowitz attempted to establish a relation between plasticity and work expended in milling. Griffiths studied the influence of the size of batch, temperature, etc., on plasticity. The Goodyear Tire and Rubber Company Laboratories investigated the influence of the temperature during milling on mastication. Shoaff determined the energy expended in mastication. Bachmann, Behre and Blankenstein made a study of the dependence of the mastication on the spacing of the mill rolls, on the speed of the rolls, and on other factors. Finally Busse and Cunningham investigated the dependence of plasticity on the temperature of mastication and on atmospheric oxygen.

The experiments described in the present work show that it is very important in making measurements of mastication effects to distinguish between permanent softening of the rubber and the softening brought about solely by the effect of heat. In the work described, the experimental conditions were maintained rigidly constant.

The mill rolls were 200 mm. in diameter, and their distance apart could be adjusted to 1 mm. by a suitable mechanism. The size of each batch of rubber was 500 grams, and samples were removed at various intervals during mastication. By adjusting the guards to the proper distance apart, the bank of rubber between the rolls was maintained 10 mm. thick, as desired. First-latex crepe was chosen for the investigation; plasticity measurements were made with a Williams plastometer at 70° C, and the compression and elastic recovery of a test-specimen of 1 cubic centimeter were measured by this instrument.

Milling was carried out at temperatures of 20°, 40°, 60°, 80° and 100° C, and in turn with roll frictions of 1 : 1, 1 : 1.53, 1 : 2.07 and 1 : 2.58, respectively. The temperature of the mill rolls was controlled automatically. The front roll had a surface speed of 7.56 meters per minute. In all the experiments, the electric power consumed was recorded in kilowatts.

The experimental results are summarized in Table 1, and in Figures 1, 2 and 3. In Figure 1, plasticization is shown as a function of the temperature

* Translated for Rubber Chemistry and Technology from *Kautschuk*, Vol. 18, No. 11, pages 144–145, November 1942. This paper was published originally in the *Revue générale du caoutchouc*, Vol. 19, pp. 183–188 (1942), and as published in *Kautschuk*, the original paper has been greatly condensed. Since the original paper will be unavailable for an indefinite time, utilization has been made of the condensed version in *Kautschuk*.

TABLE 1

Temperature	Mill friction ratio	Plasticity (height in mm.) minutes 10	20	30	40	50	60	70	Elastic Component (increase in height in hundredths of a mm.) minutes 10	20	30	40	50	60	70
20° C	1 : 1	3.52	2.32	2.08	1.93	1.82	1.71	...	44	10	6	7	7	6	...
	1 : 1.53	2.90	2.29	2.00	1.90	1.82	1.81	...	30	10	7	5	5	3	...
	1 : 2.07	2.97	2.34	2.12	2.04	1.96	1.94	...	29	9	8	6	7	7	...
	1 : 2.58	2.81	2.72	2.16	2.09	1.90	2.00	...	23	10	8	6	6	5	...
40° C	1 : 1	2.88	2.37	2.24	2.12	2.02	2.01	...	28	11	9	7	7	7	...
	1 : 1.53	3.03	2.33	2.24	2.12	2.07	2.04	...	39	9	9	7	5	5	...
	1 : 2.07	2.93	2.50	2.24	2.15	2.10	2.07	...	25	12	9	8	7	6	...
	1 : 2.58	2.76	2.43	2.33	2.34	2.14	2.13	...	21	10	9	7	8	8	...
60° C	1 : 1	3.13	2.70	2.42	2.29	2.32	2.30	...	31	13	9	8	8	9	...
	1 : 1.53	2.72	2.65	2.51	2.50	2.54	2.40	...	24	11	8	11	13	10	...
	1 : 2.07	2.76	2.48	2.55	2.56	2.40	2.40	...	16	12	10	11	13	10	...
	1 : 2.58	2.72	2.83	2.67	2.60	2.49	2.36	...	28	18	11	10	9	9	...
80° C	1 : 1	3.47	3.18	2.94	2.84	2.63	2.58	2.52	43	29	18	17	15	12	10
	1 : 1.53	3.13	3.11	2.97	2.80	2.65	2.80	2.65	39	28	26	14	12	14	11
	1 : 2.07	3.40	2.99	2.82	2.70	2.70	2.62	2.58	37	23	14	10	12	10	9
	1 : 2.58	3.10	3.09	2.84	2.68	2.63	2.60	*	25	25	17	13	12	11	*
100° C	1 : 1	3.52	3.35	3.17	3.00	3.01	2.85	2.73	40	28	23	19	18	17	14
	1 : 1.53	3.04	3.22	3.18	2.95	2.81	2.73	2.70	43	28	25	20	14	14	13
	1 : 2.07	3.52	3.27	3.07	2.84	2.77	2.70	*	42	25	18	19	14	11	*
	1 : 2.58	3.23	3.02	2.80	2.80	*	*	*	33	19	14	13	*	*	*

* Signifies tacky.

TABLE 2

Temperature	Friction	Applied electric power in kilowatts minutes 2	5	10	20	30	40	50	60	70
20° C	1 : 1	4.8	5.0	4.8	4.0	3.8	3.5	3.5	3.4	
	1 : 1.53	5.6	5.7	4.8	4.0	3.9	3.7	3.4	3.2	
	1 : 2.07	5.5	6.3	5.9	4.9	4.2	3.7	3.5	3.3	
	1 : 2.58	6.2	6.5	5.9	5.0	4.3	3.9	3.7	3.5	
40° C	1 : 1	3.2	3.4	3.4	3.0	2.6	2.5	2.3	2.2	
	1 : 1.53	4.2	4.3	3.6	3.2	2.8	2.5	2.1	2.0	
	1 : 2.07	4.5	4.5	3.8	3.2	2.85	2.75	2.4	2.3	
	1 : 2.58	5.6	5.4	4.3	3.6	3.1	2.7	2.6	2.5	
60° C	1 : 1	4.0	4.0	3.1	2.6	2.6	2.5	2.3	2.3	
	1 : 1.53	4.7	4.4	3.5	2.7	2.6	2.4	2.0	2.0	
	1 : 2.07	4.2	4.2	3.5	3.0	2.8	2.7	2.5	2.4	
	1 : 2.58	4.5	4.6	3.7	3.2	3.0	2.9	2.7	2.6	
80° C	1 : 1	3.2	3.2	2.9	2.7	2.5	2.5	2.2	2.0	2.0
	1 : 1.53	3.4	3.4	3.0	2.7	2.5	2.3	2.1	2.1	2.1
	1 : 2.07	4.0	3.9	3.3	3.3	3.0	2.8	2.7	2.6	2.6
	1 : 2.58	4.4	4.2	3.8	3.1	3.1	2.9	2.8	2.7	2.7
100° C	1 : 1	3.4	3.4	3.1	2.9	2.8	2.8	2.7	2.7	2.6
	1 : 1.53	3.6	3.5	3.2	3.2	3.1	3.0	2.8	2.7	2.7
	1 : 2.07	4.2	4.0	3.6	3.5	2.8	2.7	2.7	2.7	
	1 : 2.58	4.2	4.0	3.7	3.3	2.8	2.6	2.6		

and of the friction ratio of the mill rolls. Figure 2 shows the relation between the temperature and the energy consumed. Figure 3 shows the relation between the friction ratio and the energy consumed. The values which are given for the consumption of electricity in kilowatt-hours are based on a constant plasticity of 2.75.

The friction ratio has apparently no influence on plasticization when the latter is carried out between 20° and 80° C. There seems to be a "critical point" at 60° C, as is evident in Figure 1, and as indicated by other phenomena. At 60° C the curves of the various friction ratios cross one another at a plasticity value of approximately 2.5. At 100° C plasticization progresses rather

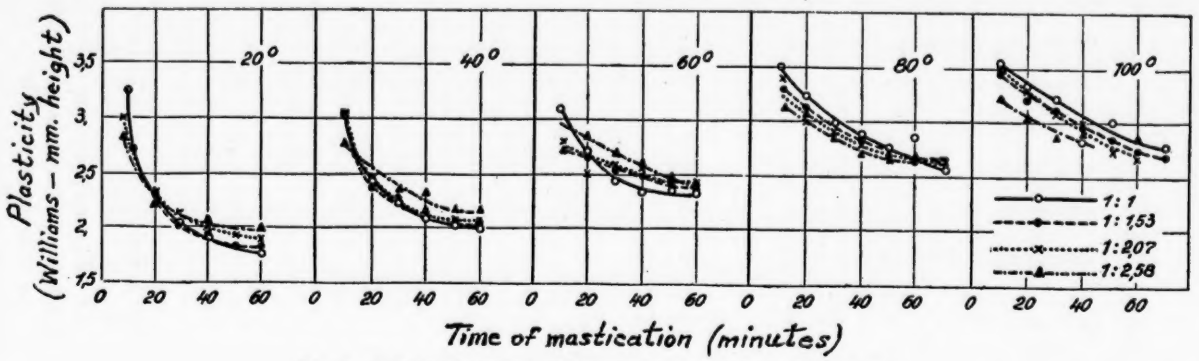

FIG. 1.—Relations between plasticity, temperature and roll friction ratio.

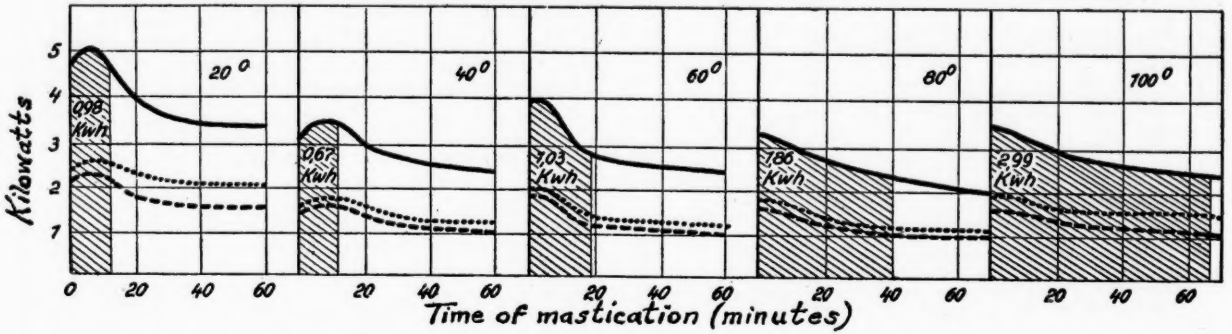

FIG. 2.—Power consumption (in kilowatts) and temperature of mastication, with friction ratio of 1. Dotted lines = power consumption of back roll; broken lines = power consumption of front roll.

Kilowatts

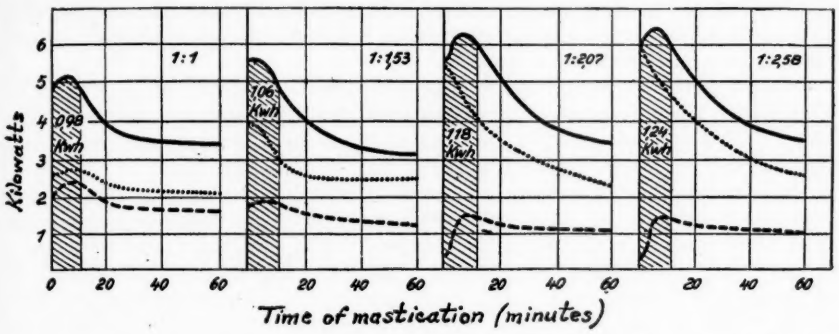

FIG. 3.—Electric power consumption (in kilowatts) and roll friction ratio Temperature = 20° C.

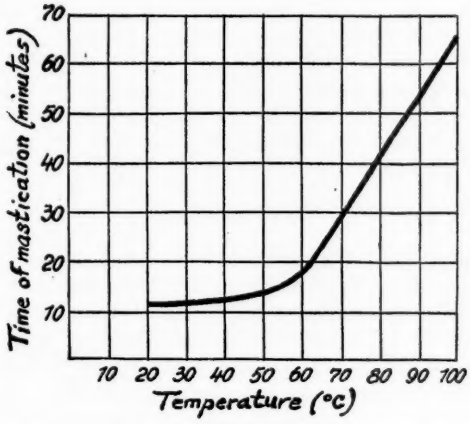

FIG. 4.—Time of mastication as a function of temperature to reach plasticity of 2.75 (Friction ratio = 1).

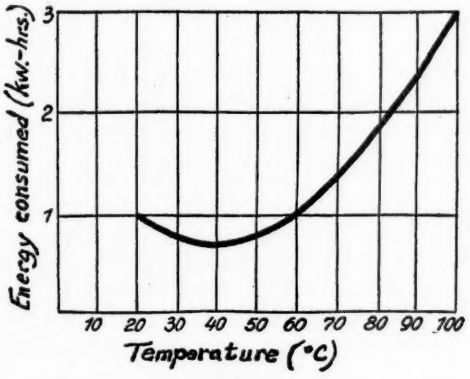

FIG. 5.—Energy consumption (kilowatt-hours) as a function of roll temperature.

Dotted lines = power consumption of back roll; broken lines = power consumption of front roll.

slowly, and in this temperature range it is apparently more accelerated than at lower temperatures by the friction ratio. The friction ratio appears to have no influence on the elastic aftereffect.

On the contrary, temperature has a considerable influence on plasticization. The higher the temperature of mastication the smaller the increase in plasticity. This is in accord with the work of Busse and Cunningham[6], who found that the rate of plasticization reached a minimum at 120° C.

It is interesting to note the times of mastication to reach a plasticity of 2.75 (see Figure 4). A sharp increase in the time of mastication appears only after the temperature of 60° C is reached. It is ordinarily assumed that a rubber stock which has been mixed at a relatively low temperature has poorer physical properties after vulcanization than the same stock which has been mixed relatively hot. However, the fact is frequently overlooked that, under these conditions, the two mixtures do not reach the same degrees of plasticity. Furthermore the temperature of milling has a great influence on the elastic component, and above 60° C this influence is manifest in the fact that the plasticized mixtures have more "nerve".

The amount of energy expended to reach a plasticity value of 2.75 increases with increase in the friction ratio of the mill rolls. However, a comparison of the amounts of energy expended at different temperatures shows that above 60° C the amount of energy expended to reach a definite degree of plasticity increases rapidly with increase in temperature. At 40° C there is a well defined, though not sharp, minimum amount of energy expended (see Figure 5).

REFERENCES

[1] Grundy and Schidrowtiz, English patent 15, 438 (1915).
[2] Griffiths, *Trans. Inst. Rubber Ind.* 1, 308 (1926).
[3] Goodyear Tire and Rubber Co., in "Vanderbilt Rubber Handbook", 1929, p. 58.
[4] Shoaff, *Rubber Age* (N. Y.) 23, 142 (1928).
[5] Bachmann, Behre and Blankenstein, *Kolloid-Z.* 57, 67 (1931).
[6] Busse and Cunningham, *Proc. Rubber Tech. Conf. London*, 1938, p. 288.

TREAD CRACKING OF NATURAL AND SYNTHETIC RUBBER STOCKS *

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The development of cracks in the base of the tread grooves of tires has long been recognized as a major factor governing their useful life. A number of laboratory tests have been employed in an effort to evaluate crack initiation and growth. Dumbbell strips[1], rings[2], and grooved blocks[3] have been flexed through various tension cycles. Grooved belts[4] and tire treads[5] have been flexed by weaving over pulleys and thereby producing a cycle which involves both tension and compression. Tires themselves have been flexed under load on rotating drums[6].

The strains which produce cracking along the length of a tire groove are complex[7]. They occur on and near the surface in the base of the groove. For the purpose of this discussion, they are defined as the strains at right angles to the groove length and in the plane of the groove base. To devise a flexing machine which reproduces these strains qualitatively, one must consider the forces acting to produce them.

The force acting upward on the ribs of the tire tread in the contact region bends the tread to an extent which is determined primarily by the load on the tire, the inflation pressure, the moulded tire shape, and the fabric structure. This bending is concentrated to a large extent in the groove base, with its magnitude substantially independent of the speed of the tire and of the tread stock used; and a compression strain of constant amplitude is produced. This upward force also deforms the ribs and thus contributes a slight additional compression strain of the constant force type. This produces little difference in the compression strain between different stocks, especially since all normal tire treads have moduli in the same general range. Compression strains of the order of 30 per cent have been found in the base of the grooves of passenger tires under static load by means of cement casts of the grooves in which wire brads were embedded as markers[8].

When the tread section in question leaves the road surface, tension is introduced as a result of the bending caused by centrifugal force. Thus the rubber in the base of the groove passes from compression, through zero strain, into tension. An additional tension is probably introduced by the outward displacement of the tread, observed as a bulge noticeable at high speeds at a point immediately adjacent to the contact area. In neither case does this tension depend to any significant extent on the tread stock, although it increases with increase in tire speed. Thus, for any given tire speed, it may be considered to be of the constant amplitude type. The predominance of the constant amplitude type of strains justifies the use of a constant amplitude flexing test for laboratory evaluation.

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Flexing mechanism on the groove cracking machine.

The inclusion of compression and zero strain to tension in the flexing cycle of tread type stocks affects the flexing resistance[9]; this indicates their desirability in a laboratory evaluation test. The compression element of the cycle also serves to eliminate the change in the flexing cycle caused by permanent set[10] during the progress of a test involving only tension. Thus the groove cracking machine used in this work was developed to produce, with a simple test-piece, a flexing cycle which includes both tension and compression. The maximum tension was increased somewhat over that normally encountered in a tire to reduce the flexing time to a reasonable value.

TENSION-COMPRESSION FLEXING

The test-piece normally used in the groove-cracking machine is shown in Figure 1. It was one of four obtained from a cured slab by slicing in a direction perpendicular to the moulded groove. Twelve such test-pieces could be flexed in the machine at once in six independent units holding two test-pieces each. The six units with the test-pieces clamped in place are shown in the photograph. For smooth operation, the six units were arranged in a balanced "firing" order. The test-pieces were clamped in place one unit at a time.

To clamp the samples, the unit to be loaded was secured in its closed position by a locking pin in the flywheel (covered in the picture) at the left-hand end of the cam shaft. The test-piece was positioned over centering pins

located in the lower jaw. The Allen screws were then drawn down with alternate one-quarter turns until they were tight against the upper boss. The screws forced the pivoted upper jaws down on the faces of the test-piece, reducing the 0.5-inch (1.27-cm.) thickness of the test-piece to 0.4 inch (1.02 cm.) in the clamped region. With the standard test piece this procedure introduced a compression of 43 per cent in the base of the groove. Although, by inserting the pin joining the connecting rod to the vibrating jaw mechanism in different positions, any one of five flexing cycles could be obtained, the ma-

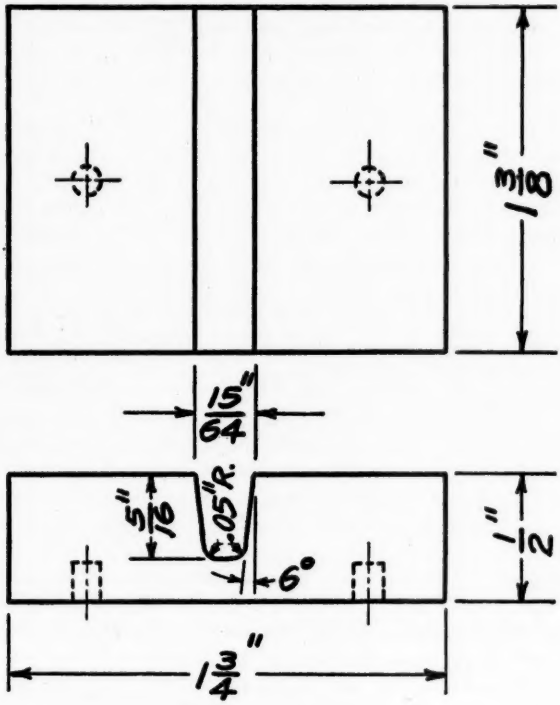

FIG. 1.—Test specimen.

chine was so designed that the closed position remained the same. Thus only the maximum tension component of the flexing cycle varied, the maximum compression component remaining at 43 per cent. This change in amplitude of the flexing cycle of the machine corresponds closely to a change in speed of a tire in service where the maximum tension changes but the maximum compression remains relatively constant. The maximum strains of the five settings are as follows:

Setting	Tension (%)	Setting	Tension (%)
A	21.5	*D*	64.5
B	30.0	*E*	93.0
C	44.5		

Because of the slight bending given the test-piece as a result of the pivoted motion of the vibrating jaw, the bottom of the test-piece received slightly less maximum tension than the base of the groove.

The flexing cycles of the twelve-station machine were selected to give reasonable testing times for all types of tread stocks, natural and synthetic. (Preliminary studies of flexing cycles had been conducted on an experimental two-station machine in which the amplitude and pivot position of the vibrating jaw could be adjusted to any value desired.) The cam shaft, operated in an oil bath, was driven by one of two motors. The main motor in line with the shaft operated at 1160 r.p.m., the normal flexing speed. A lower motor-gear reducer assembly rotated the shaft at a speed of 57 r.p.m. Upon completion of construction of an oven to enclose the vibrating mechanism, it is planned to use this motor to flex the samples slowly during the warm-up period in elevated ambient temperature tests to ensure equal conditioning of all samples. All tests here reported were made at a room temperature of 28° ± 2° C.

Both precut and uncut samples were tested. The precut, 0.2 inch long and 0.047 inch deep (0.508 × 0.119 cm.), was placed in the base of the groove, parallel to it, and midway from its ends. To make the cut, a knife was drawn the length of a slotted guide with the shoulders of the knife in contact with the guide, and with the guide firmly pressed against the base of the groove. Water was used to lubricate the knife. To prevent cracks from starting at the ends of the groove of an uncut sample, the ends were seared with a hot iron rod (slightly cooler than dull red) drawn across the upper edge of the groove base at an angle of 45° to the base. This technique eliminated the discrepant results sometimes found for the flexing of uncut samples. Similar erratic results have been reported by others[11].

Two types of cracking tests resulted from the use of the two kinds of test-pieces—crack-growth tests from the precut samples and crack-initiation tests from the uncut samples. In the crack-initiation tests, measurements were made at the beginning and at the completion of cracking, *i.e.*, the point at which the block broke completely in two. By means of this latter method of measurement, a combination of crack-initiation and crack-growth was obtained.

The shape of the test-piece made possible the flexing of samples obtained directly from tires. To make stock comparisons independent of groove shape, the groove shape of the tire sample was duplicated in a laboratory control sample; a plaster of Paris cast of the tire sample groove was obtained, which, in turn, was used to form a plaster of Paris mould. From this mould a tin ribbed insert could be cast for use in an auxiliary rubber mould of the same dimensions as the prepared tire sample. Studies of various groove shapes could be made by using a test-sample mould in which ribs of various shapes were inserted.

All cracking studies reported were conducted on the basis of the time necessary to produce a selected degree of cracking. This type of measurement placed the results on a semiquantitative basis. In routine testing, where qualitative results were usually sufficient and the time consumed by the operator became a factor, the amount of cracking in a given time was used as the index of evaluation. This latter test was not quantitative in the case of widely divergent stocks in which one block cracked in two before any perceptible growth had taken place in the other.

GROOVE CRACKING OF TREAD STOCKS

The increasing interest in blends of various natural and synthetic rubber polymers suggested the desirability of studying the cracking resistance of tire-tread stocks made from them. Blends of Hevea plus GR-S, guayule plus

GR-S, reclaim plus GR-S, and Hevea plus reclaim were selected. Four basic formulas were used for these blends (Table I). Master batches of each of these stocks were mixed, with the sulfur omitted. The master batches were blended in the proportions desired, based on the weight of the polymer. (The proportions of reclaim were based on the rubber hydrocarbon present. For the reclaim used, analysis showed 192.3 parts by weight to contain 100 parts of

TABLE I

BASIC FORMULAS (PARTS BY WEIGHT)

Pigment	Hevea smoked sheet	GR-S (75 butadiene–25 styrene)	Guayule (unde-resinated)	Reclaim (whole tire)
Polymer	100	100	100	192.3
Sulfur	3	2	3.5	3
Zinc oxide	3	5	3	3
Stearic acid	3.5	3	1	3
Captax	1	1.5	1.5	1
Bardol	3	5	...	3.5
Neozone-D	1	1	1	1
Channel black	50	50	50	20.5

rubber hydrocarbon.) Sufficient sulfur was added to equal the amount of sulfur which would have been present had the total stocks been mixed and blended in similar proportions. It should be noted that the mixing was more thorough than that usually obtained from normal laboratory or factory procedure. The flex-cracking tests should be interpreted accordingly, particularly in the case of GR-S crack-initiation tests, since good channel black dispersion may materially aid flexing resistance. Tensile tests were made over a range of cures to select the optimum (Table II) for use in stock comparisons.

TABLE II

CURES USED IN STOCK COMPARISONS

Parts by weight of polymer				Cure at 137.8° C (280° F) (min.)
Hevea	Guayule	GR-S	Reclaim	
100	...	...	...	60
50	...	50	...	60
20	...	80	...	90
10	...	90	...	90
...	...	100	...	120
...	50	50	...	90
...	100	...	...	60
80	...	...	20	40
50	...	...	50	40
10	...	...	90	40
...	...	...	100	40
...	...	50	50	60

To compare the effect of the five amplitudes of vibration of the machine (*A* to *E*) on crack growth, the 50 Hevea–50 GR-S stock was studied. The flexing time necessary for the precut sample to grow 0.3 inch (0.72 cm.) in length is plotted against the maximum tension in Figure 2. For convenience the flexing times of all groove-cracking tests are plotted on a logarithmic scale. Figure 2 shows that it was possible to obtain a wide range of flexing times on the machine, and that the decrease in flexing time with increase in maximum tension proceeded at an orderly but decelerating rate. (Of interest in this connection was an unpublished cracking test, conducted by the author several

years ago, of a typical Hevea tread stock, using the original two-station experimental machine with a specimen somewhat larger than the present one. Precut samples were flexed through three different cycles: 65 to 22% tension, 65% tension to 8% compression, and 65% tension to 26% compression. The relative rates of crack growth were 9, 61, and 270, respectively. Taken to-

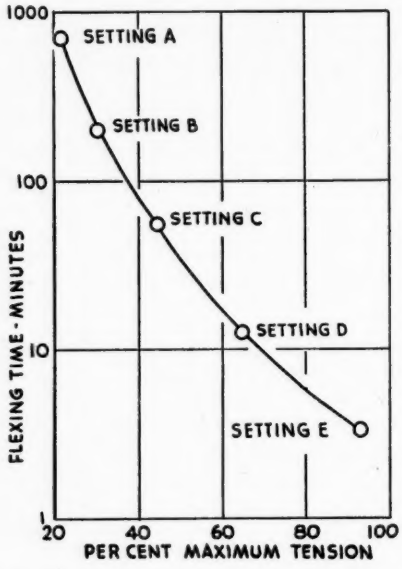

FIG. 2.—Effect of amplitude on crack growth (time to crack 0.3-inch; sample of 50 Hevea–50 GR-S tread stock).

gether, these tests show that a decrease in flexing time, for a given crack-growth, may be obtained by increasing the amplitude at either end of the flexing cycle. They also indicate the significant effect on the flexing life of allowing the flexing cycle to pass through zero strain.)

Since the temperature of the test-specimen is known[12] to affect greatly its flex-cracking resistance, measurements of the temperature build-up were obtained for the five machine settings, using uncut samples of the 20 Hevea–80 GR-S stock. These measurements were made during flexing with a No. 36, B. & S. copper-constantan thermocouple pressed against the base of the groove by means of a thin Bakelite rod wrapped with friction tape. The equilibrium temperature rise for each setting, established after 10 minutes of flexing with the thermocouple in place, was as follows: *A*, 45° C; *B*, 58°; *C*, 70°; *D*, 85°; *E*, 101°. The increase in temperature rise found with increase in flexing amplitude undoubtedly contributed to the large decrease in crack growth resistance shown in Figure 2.

The effect of cure on elongation at break, tensile strength at break based on the original section, and crack growth were studied for Hevea and GR-S stocks (Figure 3). For both stocks, the cure for optimum resistance to crack growth was found to be lower than that for optimum tensile strength.

The physical properties obtained on the blended stocks are presented in Figure 4. Temperature rise values for test-specimens of the four basic stocks

(setting *C*) were as follows: Hevea, 68° C; GR-S, 76°; guayule, 86°; reclaim, 63°. The results of these blend comparisons may be summarized as follows:

The Hevea-reclaim stocks decreased in flexing life with increase in reclaim for both crack-growth and crack-incipience tests. In crack-growth tests, the

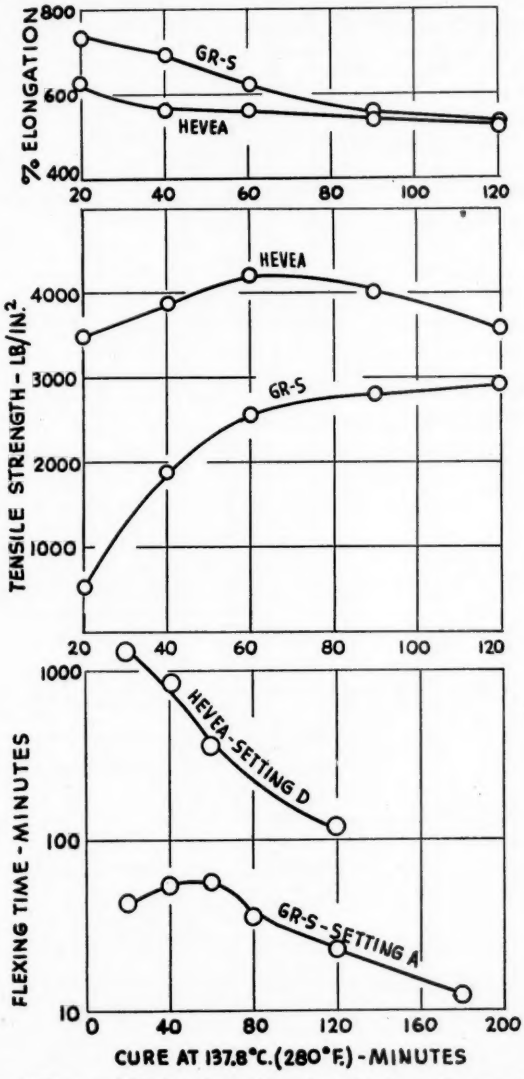

FIG. 3.—Effect of cure of Hevea and GR-S stocks on elongation at break, tensile strength, and crack growth. (Time to grow 0.3-inch; precut samples.)

Hevea–GR-S, guayule–GR-S, and, to a lesser extent, reclaim–GR-S stocks decreased in cracking resistance with increase in GR-S. In crack-incipience tests, these same stocks increased in cracking resistance with increase in GR-S. Minor deviations from these generalizations occurred: The crack-growth of

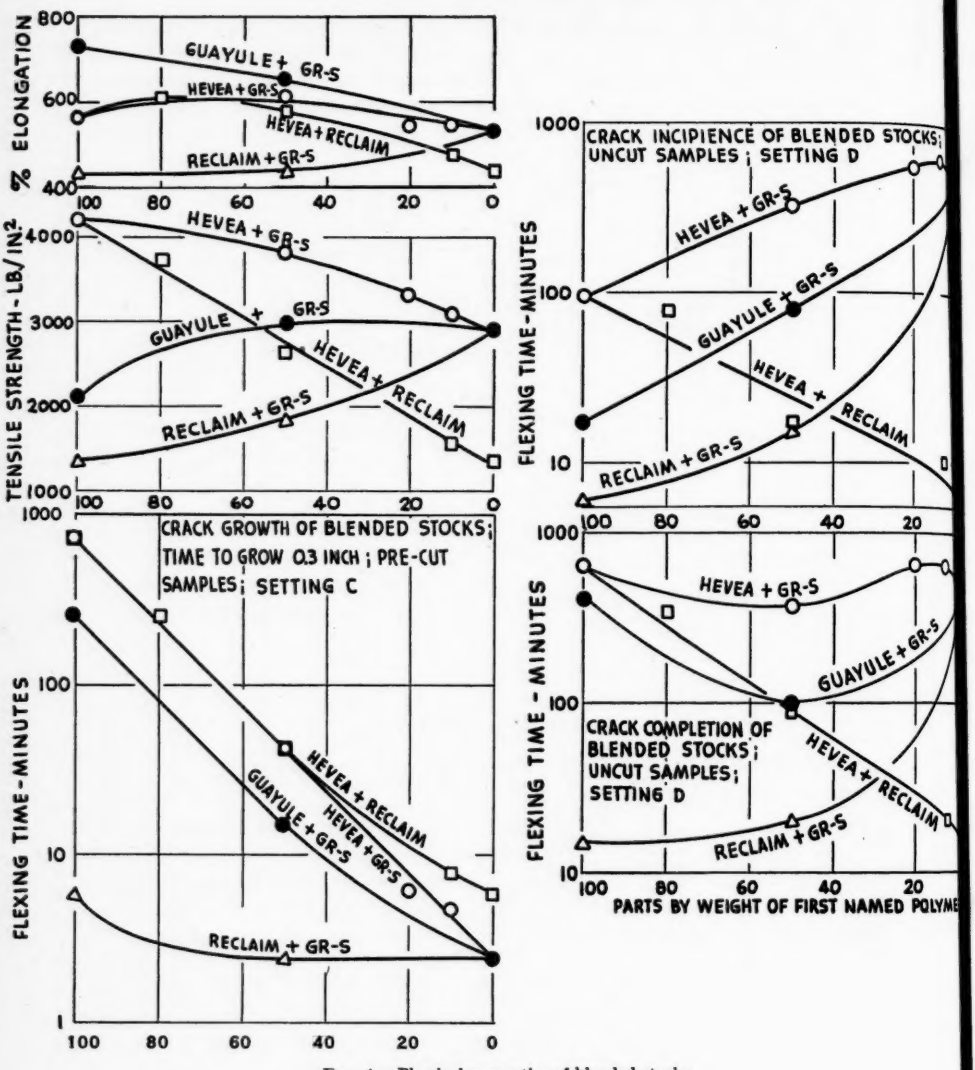

FIG. 4.—Physical properties of blended stocks.

reclaim–GR-S stocks remained constant between 50 and 100 parts of GR-S; and an optimum cracking life existed for the 10 Hevea–90 GR-S blend in crack-incipience tests.

When the crack-initiation tests were continued to completion of cracking, the results were found to be similar to those of the same blocks at incipience of cracking, except that the Hevea and guayule increased in cracking resistance to values approximately equal to that of GR-S. In other words, in the case of Hevea and guayule, a considerable flexing interval was found between the time small cracks first appeared and the time the blocks were completely cracked. In the case of all other stocks tested, the blocks broke in two very soon after cracks were first observed.

Tensile strength was found to correlate with neither crack-initiation nor crack-growth.

Inspection of the cracks in Hevea and GR-S revealed a fundamental difference in appearance similar to that observed in tear tests[13]. The cracks in the Hevea were forked and curled, typical of the condition described as knottiness. The cracks in the GR-S were straight and regular, with no apparent tendency toward knotting.

IMPLICATIONS OF RESULTS

It was apparent from these results that a marked difference existed between tests of crack-initiation and crack-growth of stocks containing GR-S. This may resolve apparently contradictory statements in the literature[14], and explains why GR-S stocks resist cracking in some types of service but succumb to it in others. Since, in most types of service, minute cuts and abrasions normally are introduced into the base of the grooves of a tire, it is suggested that crack-growth tests on the groove-cracking machine provide the more reliable index of tire groove-cracking. From an analysis of the crack-growth tests of the blended stocks, certain suggestions may be ventured regarding the probable effect of mixing various polymers:

1. The addition of a small amount of Hevea to a Gr-S tread stock (say 10%) appreciably increases flex-cracking life. Conversely, the addition of a similar amount of GR-S to a Hevea tread stock decreases cracking life.
2. Similar results may be anticipated where guayule is substituted for Hevea, or reclaim for GR-S.
3. Reclaim and GR-S may be blended in any proportion with relatively little change in flex-cracking resistance. Some superiority in the case of high-percentage reclaim stocks is indicated.
4. The order which might be anticipated for cracking of tires made from the single polymer stocks studied, in order of decreasing merit, is: Hevea, guayule, reclaim, and GR-S, with little choice between the latter two.

The contrast between the 280-to-1 superiority of the Hevea to GR-S in crack-growth tests and the 4-to-1 superiority of GR-S to Hevea in crack-initiation tests measured at incipience of cracking is striking. In view of the close similarity in appearance between test-samples submitted to cracking and to tear tests, it is suggested that the same physical properties of the stocks influence both. It seems clear that the physical properties producing knottiness in Hevea stocks are responsible, at least in part, for its superior crack-growth resistance to that of GR-S.

Although a short time and a moderate ambient temperature were used in obtaining the cracking data, the relatively high temperatures developed within the samples during flexing (approaching those in tire treads in service) suggest the possibility that oxidative scission influenced the results to an appreciable extent. Experiments on aged and unaged samples over a range of ambient temperatures are contemplated to investigate this contingency.

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REFERENCES

[1] Cooper, *Ind. Eng. Chem. Anal. Ed.* **2**, 391 (1930); RUBBER CHEM. TECH. **4**, 134 (1931); Somerville, *Trans. Inst. Rubber Ind.* **6**, 130 (1930); Hopkins, *India Rubber World* **88**, Sept. 1933, p. 34; Busse, *Ind. Eng. Chem.* **26**, 1194 (1934); RUBBER CHEM. TECH. **8**, 121 (1934); Anonymous, *India Rubber World* **93**, Jan. 1936, p. 51; Cassie, Jones and Naunton, *Trans. Inst. Rubber Ind.* **12**, 49 (1936); RUBBER CHEM. TECH. **10**, 29 (1937); Eccher, *Gomma* **4**, 1 (1940); RUBBER CHEM. TECH. **13**, 566 (1940); Sebrell and Dinsmore, *India Rubber World* **103**, Apr. 1941, p. 45.

[2] Eccher, *Gomma* **4**, 1 (1940); RUBBER CHEM. TECH. **13**, 566 (1940).

[3] Torrance and Peterson, *India Rubber World* **80**, July 1929, p. 62; RUBBER CHEM. TECH. **2**, 525 (1929); Booth, *India Rubber World* **82**, Sept. 1930, p. 53; Rainer and Gerke, *Ind. Eng. Chem. Anal. Ed.* **7**, 368 (1935); RUBBER CHEM. TECH. **9**, 178 (1936); Vila, *Ind. Eng. Chem.* **34**, 1269 (1942); RUBBER CHEM. TECH. **16**, 184 (1943).

[4] Anonymous, *Rubber Age* (N. Y.) **26**, 542 (1930); Neal and Northam, *Ind. Eng. Chem.* **23**, 1449 (1931); RUBBER CHEM. TECH. **5**, 90 (1932).

[5] Nellen, *Rubber Age* (N. Y.) **24**, 373 (1929).

[6] Gray, Karch and Hull, *Ind. Eng. Chem. Anal. Ed.* **6**, 265 (1934).

[7] Grote, *Rubber Age* (N. Y.) **38**, 327 (1936): Eccher, *Gomma* **4**, 1 (1940); RUBBER CHEM. TECH. **13**, 566 (1940).

[8] Liska, J. W., unpublished communication.

[9] Cadwell, Merrill, Sloman and Yost, *Ind. Eng. Chem. Anal. Ed.* **12**, 19 (1940); RUBBER CHEM. TECH. **13**, 304 (1940); *Ind. Eng. Chem.* **33**, 370 (1941); RUBBER CHEM. TECH. **14**, 378 (1941).

[10] Sebrell and Dinsmore, *India Rubber World* **103**, Apr. 1941, p. 45.

[11] Vila, *Ind. Eng. Chem.* **34**, 1269 (1942); RUBBER CHEM. TECH. **16**, 184 (1943).

[12] Cadwell, Merrill, Sloman and Yost, *Ind. Eng. Chem. Anal. Ed.* **12**, 19 (1940); RUBBER CHEM. TECH. **13**, 304 (1940).

[13] Busse, *Ind. Eng. Chem.* **26**, 1194 (1934); RUBBER CHEM. TECH. **8**, 121 (1934); Patrikeev and Melnikov, *Kauchuk i Rezina* (U.S.S.R.) Dec. **1940**, p. 12; RUBBER CHEM. TECH. **14**, 863 (1941).

[14] Sebrell and Dinsmore, *India Rubber World* **103**, Apr. 1941, p. 45; Street and Ebert, RUBBER CHEM. TECH. **14**, 211 (1941); Vila, *Ind. Eng. Chem.* **34**, 1269 (1942); RUBBER CHEM. TECH. **16**, 184 (1943).

EFFECT OF DIAMETER AND SURFACE AREA OF CARBON BLACK PARTICLES ON CERTAIN PROPERTIES OF RUBBER COMPOUNDS

D. PARKINSON

Introduction.—Investigations by means of the electron microscope in the research laboratories of the Columbian Carbon Company, U. S. A., have been made on a number of particulate carbons ranging from Thermax (coarse) to Super-Spectra (fine). The results of this work have been published by Wiegand[1] and by Wiegand and Ladd[2], and a fuller account has appeared in a recent publication[3]. This booklet also includes a comprehensive review of previous work on particle size and structure and considers the role of surface area of colloidal carbons in rubber reënforcement. All the carbon blacks examined appear to consist of spherical and spheroidal particles. This is brought out strikingly in the electron micrographs, which are excellently reproduced.

The present paper records and discusses the results of tests on rubber compounds reënforced by a number of carbon blacks covering a wide range of particle size. These carbons include all the types whose particle diameters have been recorded by Wiegand, with the addition of Dixie-40 (Kosmos-40), coarse channel or impingement (Spheron-9), and fine channel (Spheron-1).

Particle size and specific surface.—Table 1 records the particle diameters and specific surfaces in sq. cm. ($\times 10^4$) per gram (square meters per gram)

TABLE 1

Carbon	Mean diameter (mμ)	Specific surface (sq. cm. $\times 10^4$ per g.)
Thermatomic black	274	10
Lamp black	97	23
Furnace black (Gastex, Furnex)	82–83	31
Fine thermal black (P-33)	74	36.5
Acetylene black (Shawinigan)	43	65
Kosmos (Dixie)-40 black	41*	63*
Statex black	34	75
Coarse impingement black (Spheron-9)	30*	86*
Medium impingement black (Standard Micronex, Kosmobile-HM and Spheron-4)	28	94.5
Fine impingement black (Spheron-1)	24*	107*
Fine color black (Super-Spectra)	13	198

of the colloidal carbons employed in the present investigation. These are for the most part taken from the papers quoted above, and should be regarded as approximate, as a high degree of accuracy is not claimed by Wiegand, and more particularly as the actual samples used for test may not have been identical in average particle diameter to those examined by the electron microscope. This remark applies in particular to lamp black, the figure of 97 mμ referring to Rubber Velvet, an American grade, whereas English lamp black was used in the present study.

The values in Table 1 followed by an asterisk were derived by an indirect method. It is found that if the particle diameter, determined by the electron microscope, be plotted against resilience, determined by the rebound value, of the corresponding vulcanizate at any particular carbon concentration, the points, with two exceptions, lie on a smooth curve. The unknown particle diameters were found by interpolation on this curve (Figure 9). It is obvious from the curve that anomalies exist and that this procedure is not always justified. It is thought to be justified in the present instance mainly because

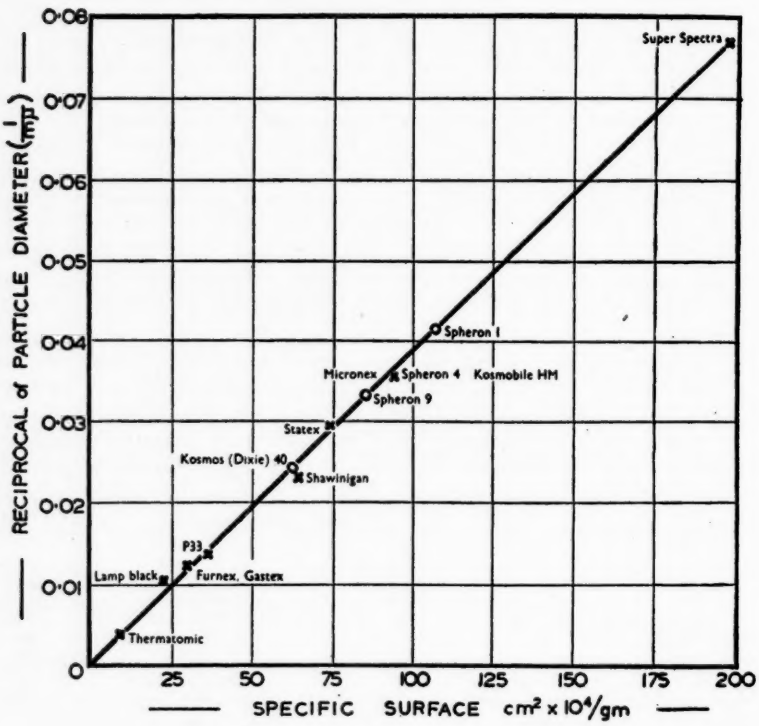

FIG. 1

the values so determined fall in the expected position on the particle diameter-abrasion curves. These curves are discussed on later pages.

An independent assessment of particle size has been made in the case of Kosmos-40. Microscopical sections of the compounds under consideration prepared by a technique previously described[4] show that this carbon gives a color by transmitted light slightly redder than that given by acetylene (Shawinigan) black, but appreciably less red than that produced by Statex. This can be interpreted as meaning that the particle diameter of Kosmos-40 lies between 43 and 34 mμ, but considerably nearer to 43, which roughly confirms the value of 41 obtained by considerations of resilience and abrasion resistance. It should be noted that the colorimetric method of comparing particle diameters is applicable only when these lie between the limits of about 30 and 80 mμ. The different channel blacks transmit a uniform reddish brown color both

when milled into rubber and when observed in colloidal suspension in a liquid, but the color transmitted by coarse channel blacks with an average diameter of 30 mμ is distinctly redder than that shown by Statex particles of 34 mμ average diameter. At the top end of the scale the gray color transmitted by

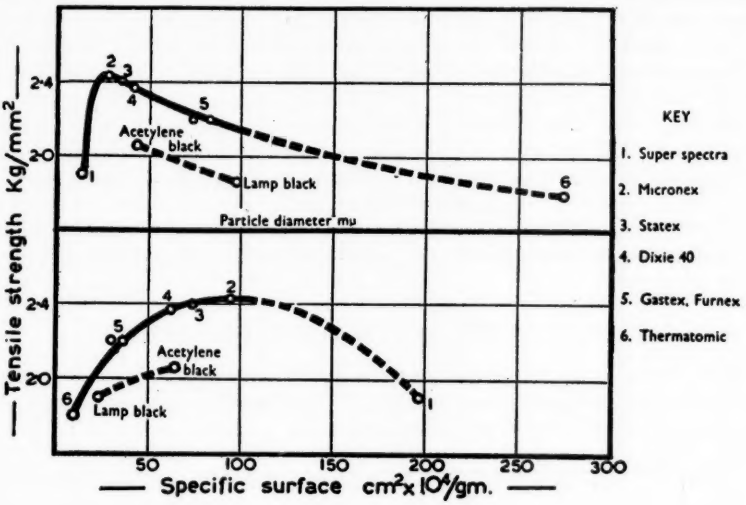

FIG. 2

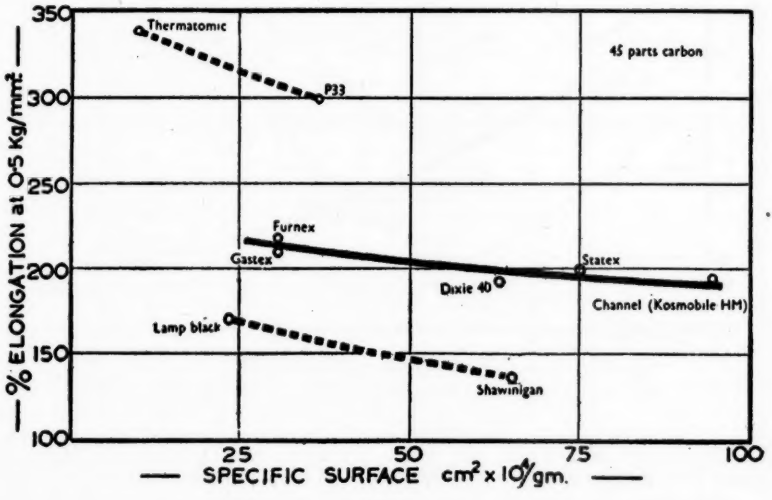

FIG. 3

rubber containing thermatomic black particles of 274 mμ is not sensibly different from that of lamp and furnace blacks in the range 100 to 80 mμ. Between 80 and 74 mμ (P-33) the particles become sufficiently small compared with the wave length of the incident light for the effects of scattering to be exhibited. As the particles get smaller a larger proportion of light is scattered and the

transmitted light becomes redder. Scattering seems to reach a limit at about 30 mμ diameter, and there is no further color change below this point.

It is interesting to note that the nigrometer also places Kosmos-40 between Statex and Shawinigan, but nearer the latter, and that it also places the impingement blacks in the right order in the carbon spectrum, to use Wiegand's term. Caution has to be used in interpreting results from this instrument, but it is useful in a qualitative sense for rapid comparisons of carbons.

Wiegand and Ladd[2] determined the specific surface by analysis of the particle size distribution curves and expressed the results in acres per pound. On Figure 1 the values used by them after conversion to sq. cm. ($\times 10^4$) per gram are plotted against particle diameter-reciprocals. They do not all lie exactly on a straight line because of differences in shape and symmetry of the distribution curves. The values of specific surface of Dixie-40, Spheron-9 and Spheron-1 used in this paper are read from this curve. Wiegand and Ladd's actual figures (converted to sq. cm. $\times 10^4$ per gram) are employed in the case of the other carbons.

PHYSICAL PROPERTIES OF VULCANIZATES

The blacks were tested at various concentrations in a base compound having the following formula: rubber, 100; sulfur, 3; mercaptobenzothiazole, 0.85; stearic acid, 3 and zinc oxide, 5 parts by weight.

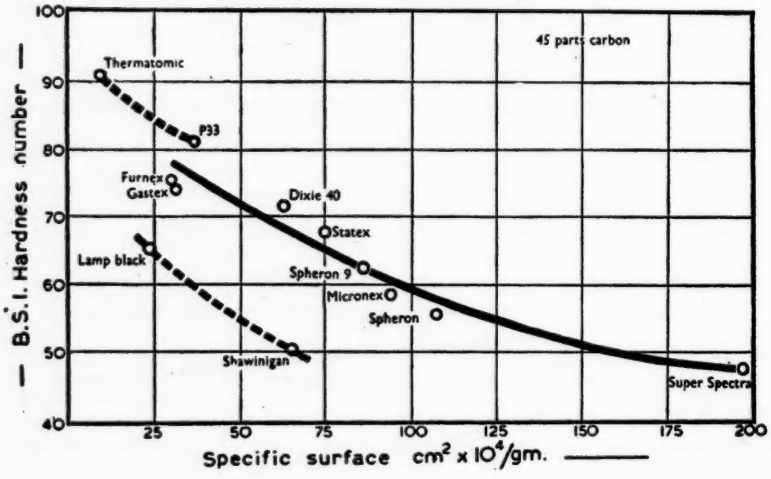

FIG. 4

Unless otherwise stated, the data are recorded at optimum cure only. This varies somewhat with the different carbons and is not necessarily the same with one property as with another. Super-Spectra gives the slowest rate of vulcanization and the nonchannel blacks the quickest, though the difference between the impingement (excepting Super-Spectra) and the non-impingement blacks is not great.

Tensile strength.—The highest values of tensile irrespective of carbon concentration are plotted against particle diameter and specific surface in Figure 2. The points, with the exception of those representing lamp and Shawinigan

blacks, lie on reasonably smooth curves, with peaks about the position occupied by the rubber grade channel blacks. The anomalous position of lamp and acetylene black is discussed later.

Stiffness.—Elongation at a given stress (50 kg. per sq. cm.) which is a measure of the stiffness of the vulcanizate, is plotted (at optimum cure and a concentration of 45 parts by weight carbon to 100 rubber) against specific

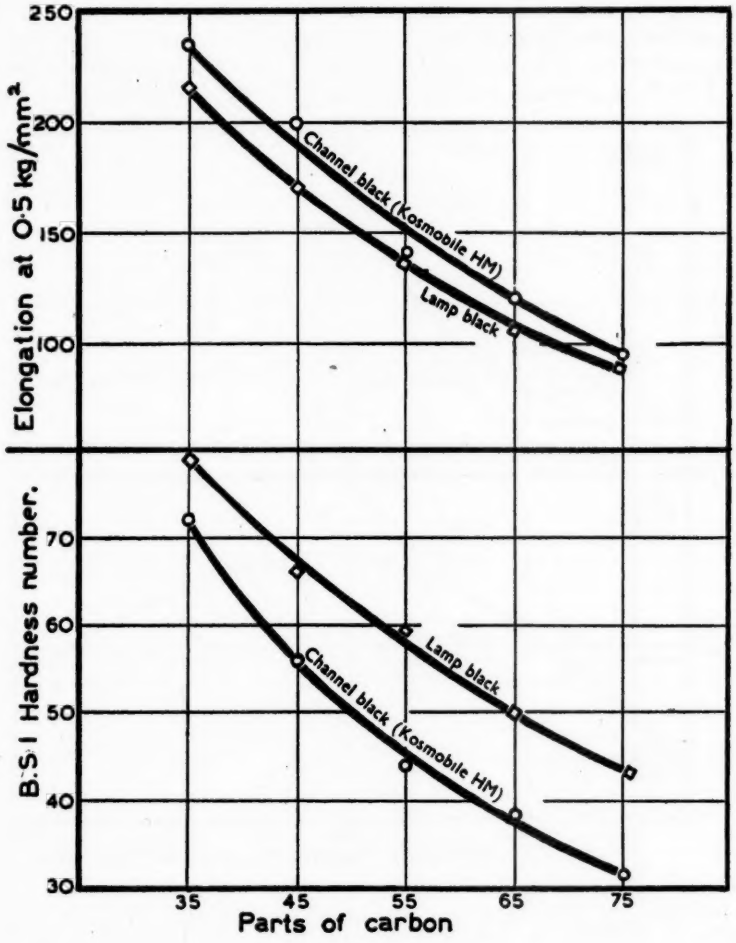

FIG. 5

surface in Figure 3. The carbons fall into three distinct series, the soft (thermal) blacks producing the most stretchy vulcanizates, with lamp and acetylene blacks forming the group of lowest stretch. Within any one series the stiffness or modulus increases with decrease of particle size. Similar curves are obtained at other black loadings.

B.S.I. hardness.—A modified form of B.S.I. tester has been developed by J. C. Hickman, and will be described in a forthcoming paper[5]. The B.S.I.

hardness numbers, of which those at 45 per cent black concentration are recorded against specific surface in Figure 4, have been obtained with this instrument. There would be little justification for the separation of the carbons into three series in the manner indicated, were it not that such an arrangement seems the most likely one in view of the evidence from Figure 3.

It will be noticed that compounds containing lamp black are less stretchy, that is, possess higher modulus, but are softer than compounds containing channel blacks. This holds throughout a range of loading from 35 to 75 by weight on the rubber (Figure 5).

Tear resistance.—The tearing tests were carried out on a form of apparatus referred to in a previous paper[6], but not yet described in detail. Tearing

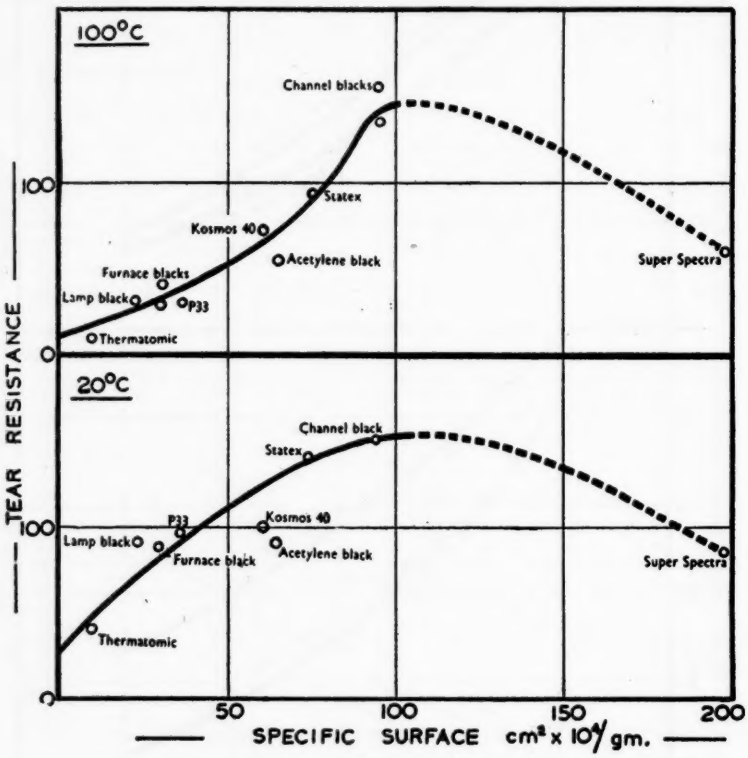

FIG. 6

resistance is difficult to measure with precision and the data recorded in Figure 6 should be regarded as approximate. This property, both at ordinary temperatures and at 100° C, depends more on type than on concentration of carbon, impingement blacks producing the best tear resistance. The test is not sufficiently sensitive to distinguish between the different rubber grade impingement blacks, but it shows the ultra-fine Super-Spectra to give poorer tearing properties than the rubber blacks. Figure 6 illustrates the approximate relationship between tear resistance at 20° C and 100° C and specific surface. The highest tear resistance values are employed, irrespective of carbon concentration.

Resilience.—For a number of years this property, which is measured as percentage rebound on the Healey pendulum, has been used in the Dunlop Rubber Company's laboratories for distinguishing between carbon blacks[7]. Recent work by Bulgin[8] had resulted in an improved accuracy of pendulum testing. This work has enabled corrections to be applied to rebound values, and it shows that resilience decreases linearly with increased carbon concen-

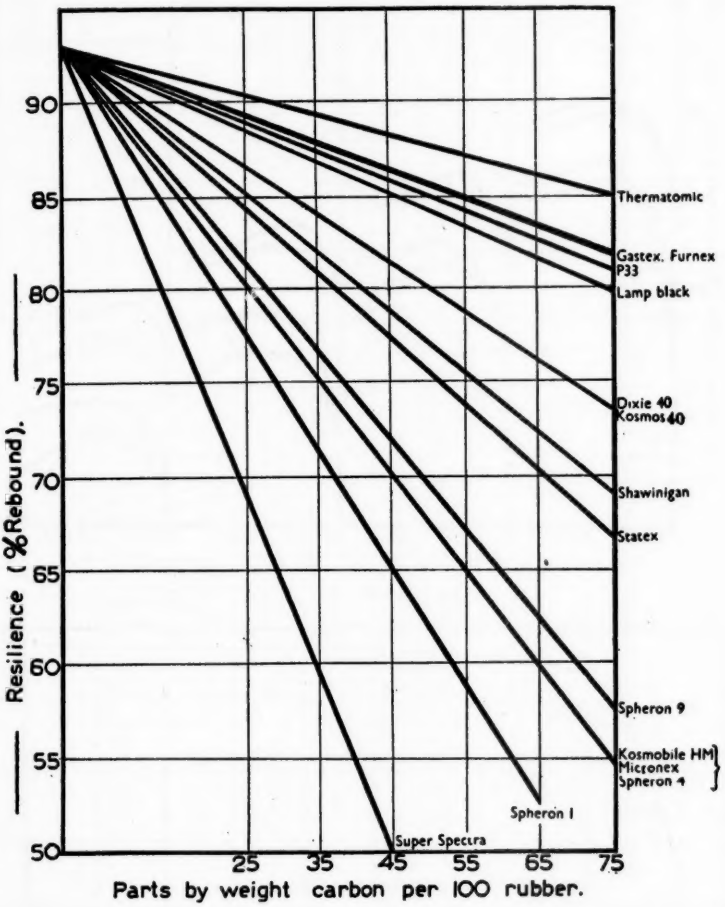

FIG. 7

tration throughout the range of ordinary compounding practice. In Figure 7 maximum resilience at 50° C is plotted against carbon concentration over the whole range of blacks. The curves show that the order of resilience follows that of particle size, with the exception of lamp and acetylene blacks.

Resilience increases with temperature to 120° C and higher, the temperature of maximum resilience depending on the type of compound and the state of vulcanization. After passing through an optimum value, it then falls as the temperature is further increased. In Figure 8 the resilience values given

by two channel blacks are compared at 50° C and 100° C over a range of compounds containing four different carbon concentrations. Although varying in particle diameter by no more than two or three millimicrons, the two blacks are readily distinguished at each concentration when tested both at 50° and 100° C.

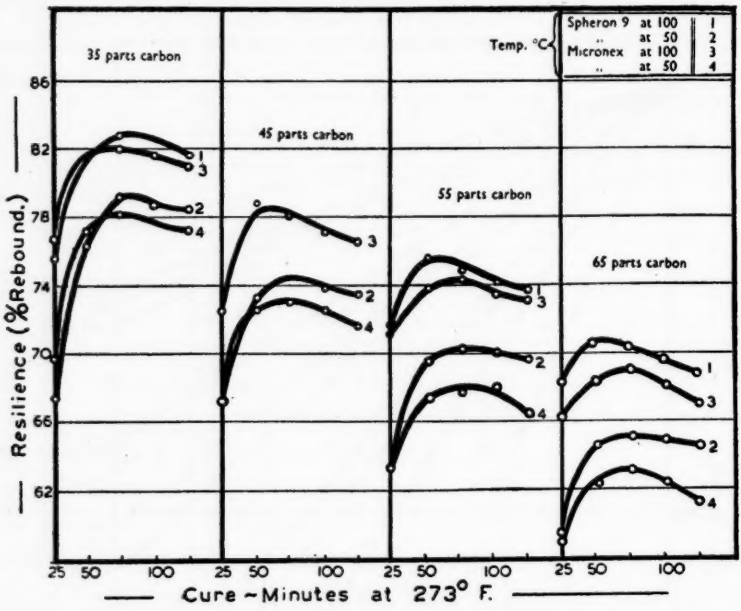

FIG. 8

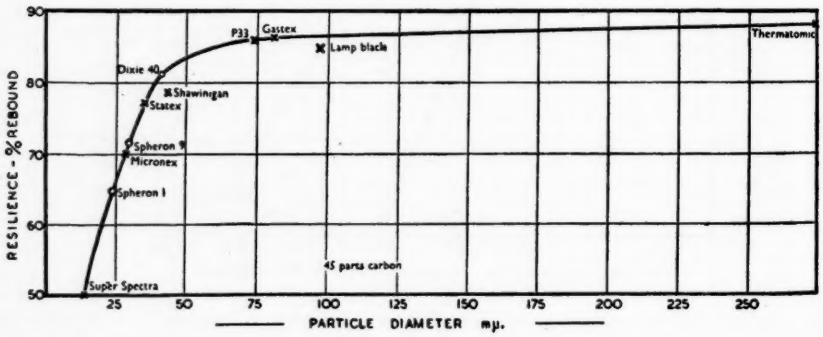

FIG. 9

Figure 9 illustrates the relationship between resilience (at 50° C) and particle diameter at 45 per cent carbon loading. The points, with the exception of those representing acetylene and lamp blacks (which promote lower resilience than is expected from the particle size) lie on a smooth curve which is approximately a hyperbola, and which shows that in the reënforcing region a small change in particle diameter produces a comparatively large one in

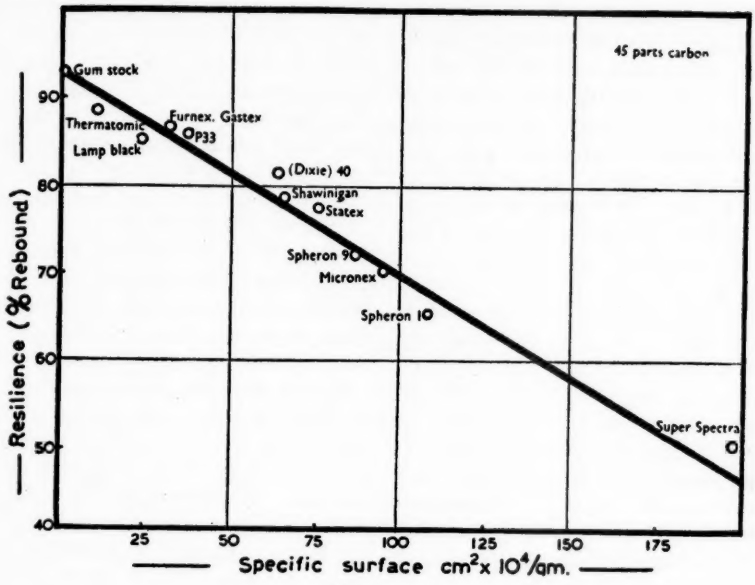
45 parts carbon
Gum stock
Thermatomic
Lamp black
Furnex. Gastex
P33
(Dixie) 40
Shawinigan
Statex
Spheron 90
Micronex
Spheron 10
Super Spectra
Resilience (% Rebound)
90
80
70
60
50
40
25
50
75
100
125
150
175
Specific surface cm²x 10⁴/gm.

FIG. 10

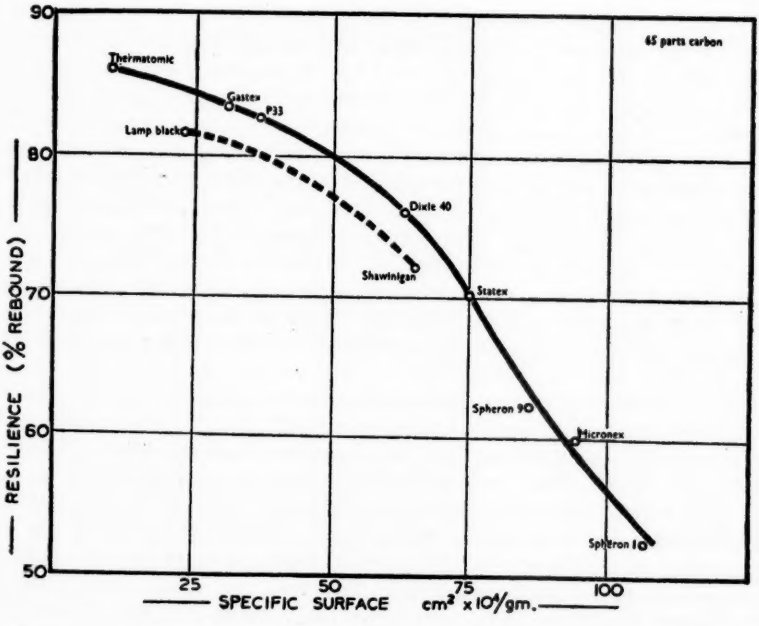
45 parts carbon
Thermatomic
Gastex
P33
Lamp black
Dixie 40
Shawinigan
Statex
Spheron 90
Micronex
Spheron 10
RESILIENCE (% REBOUND)
90
80
70
60
50
25
50
75
100
SPECIFIC SURFACE cm² x 10⁴/gm.

FIG. 11

resilience, whereas in the semireënforcing and thermal black region the change in resilience with particle size is small.

The rebound-specific surface relationship is illustrated in Figures 10 and 11 at carbon concentrations of 45 and 65 per cent, respectively. The distribution of the points in Figure 10 indicates an approximately straight line relation when the series is considered as a whole, but there is a big gap between Super-Spectra and Spheron-I which it was not found possible to explore in the present investigation. It is evident that, in detail, resilience does not vary linearly with specific surface, and it is further evident that if a smooth curve can be drawn, the points representing lamp and acetylene blacks will not be expected to fall on it, since they do not lie on the resilience-particle diameter curve. In Figure 11, therefore, a curve is drawn through the points from Thermatomic to Spheron-1, excepting those denoting Shawinigan and lamp blacks, through which a separate tentative curve is drawn. The primary curve shows that between the channel blacks and Dixie-40, through the point occupied by Statex, resilience is increasing at a greater rate than the reduction in surface. Wiegand and Ladd[2] figure a curve of similar shape. These authors state that "there appears, at least in this tentative curve, a point to inflection in the region of the rubber grade impingement carbons. A slight reduction in carbon surface at this point is repaid by marked increase in rebound resilience."

In the region of the semireënforcing and thermal blacks, resilience increases at a lower rate than the reduction in specific surface. If the upper curve in Figure 11 be produced through the point representing Thermatomic to the position of zero specific surface, it meets the resilience axis at a value of about 86 per cent, or 7 per cent below the point denoting the stock containing no carbon. The difference between these two points depends on the carbon concentration (see also Figures 10 and 12). If resilience were an exact linear function of specific surface, the two points would coincide at all carbon concentrations. There is, however, no justification in prolonging these curves beyond the points representing thermatomic carbon, as this is the region of nonreënforcement, and evidence is wanting on the effect of comparatively large spherical particles on resilience. It is, of course, theoretically impossible for the resilience-specific surface curves actually to reach the point of zero specific surface, as this point really indicates infinite particle size and not mere absence of carbon in the rubber. Practically, there is likely to be little interest in the use of spherical particles larger than one micron in diameter, which represents a surface of 60,000 sq. cm. per cc., or roughly one-third that given by Thermatomic black.

Figure 12 shows the relationship between resilience and specific surface of vulcanizates containing various mixture of different forms of carbon black with channel black (Micronex) at a total carbon concentration of 55 per cent. The "single black" compounds at the same loading are included for comparison. The points sort themselves out into three fairly distinct curves. The lamp black-gas black curve, as expected, deviates markedly from the curve passing through the "single black" points. Between these two curves lie most of the points representing mixtures of Thermatomic black, Gastex and P-33 with channel black, and one curve has been drawn through them. These curves demonstrate the expected conclusion that Statex and Kosmos-40 promote higher resilience than mixtures of impingement and semireënforcing or thermal blacks possessing equal specific surface.

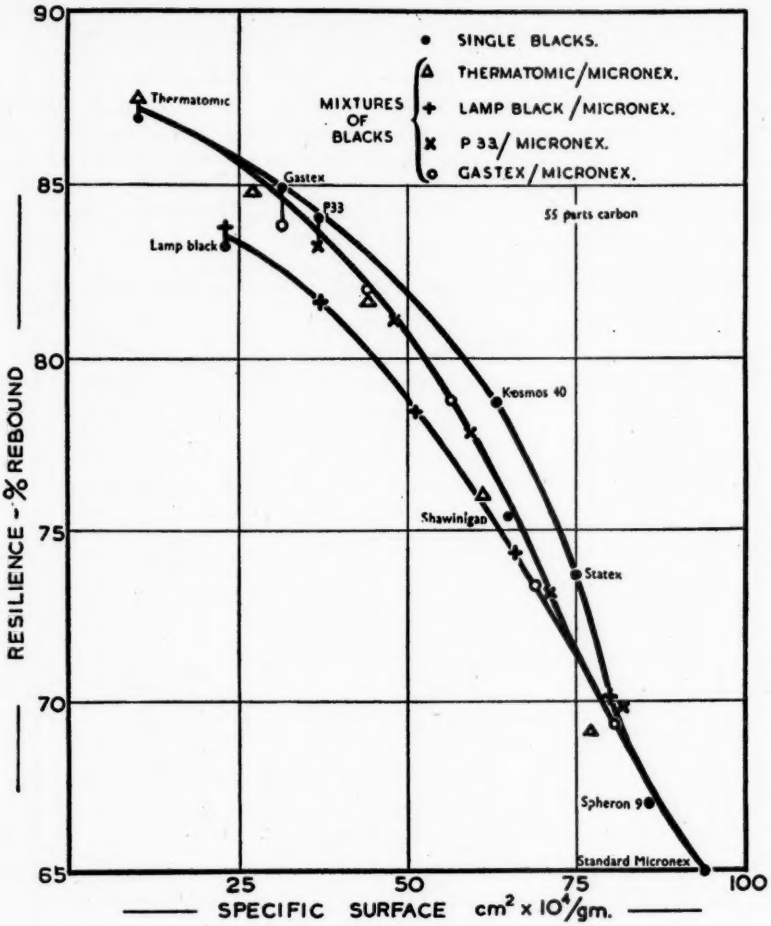

FIG. 12

Abrasion resistence.—The difficulty of correlating the results of laboratory abrasion testing with road performance is appreciated by all tire technologists, and for this reason the data presented in the present paper may be regarded sceptically by compounders and others with experience of the abrasion problem. The tests under consideration have been made on an improved modification of the Dunlop-Lambourn constant-slip machine[9], which takes account of transmitted energy in addition to slip. The improvements were initiated about ten years ago by E. F. Powell and S. W. Gough, and more recently a considerable amount of time has been devoted to the abrasion problem by S. W. Gough, who is largely responsible for the design of the present machine. Abrasion testing on this machine has agreed reasonably well, both qualitatively and quantitatively, with the results of road testing on normal types of compound. The agreement has not been quite so close quantitatively with high-reclaim stocks, which have given abrasion loss too high, and compounds con-

taining rubber extenders, which have given low abrasion loss compared with road testing. Certain types of compound are likely to give fictitiously low abrasion loss values on the machine, usually as a result of stickiness which may develop on the surface of the sample during running. Such stickiness, if present in only a minor degree, is not easy to detect. An instance of it was found in the present investigation, affecting the compounds containing Super-Spectra black. A minimum abrasion loss value of 75 (compared to 100 for rubber-grade channel black) was obtained at optimum loading, and although the results of repeat tests showed good agreement, it was observed that the

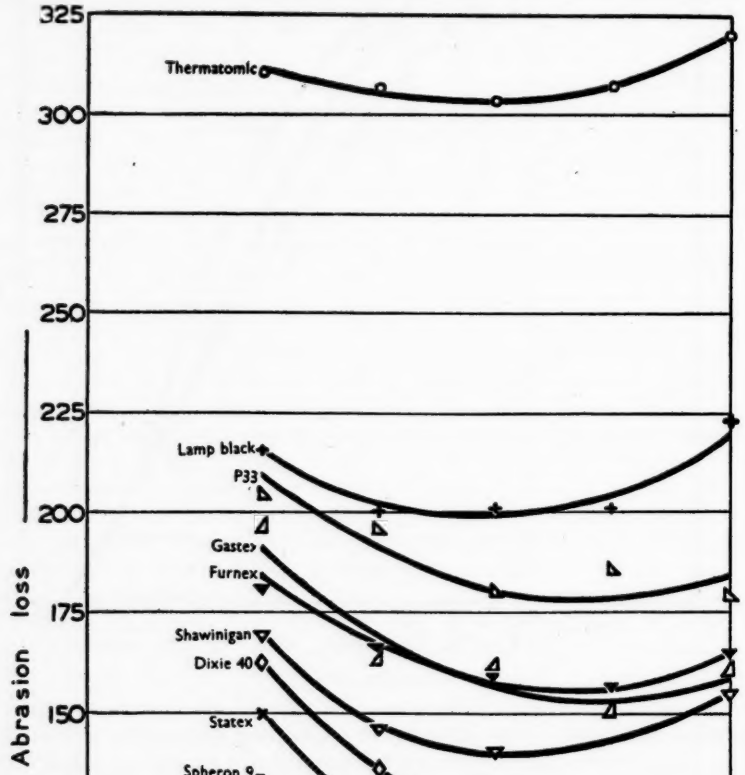

FIG. 13

specimens after testing were slightly sticky. These results were therefore discarded, and comparisons were made on a series of compounds containing diphenylguanidine (both in the Super-Spectra and control mixings) as accelerator. There was no trace of stickiness in the abraded specimens, and the minimum abrasion loss figure of 81 is considered to give an approximate reflection of the possibilities of compounds containing this black to withstand road wear provided processing difficulties can be overcome.

The abrasion loss-loading curves are recorded in Figure 13. In nearly all cases reasonably good curves can be drawn through the points, and in those cases where distribution of the points is somewhat erratic, the error involved

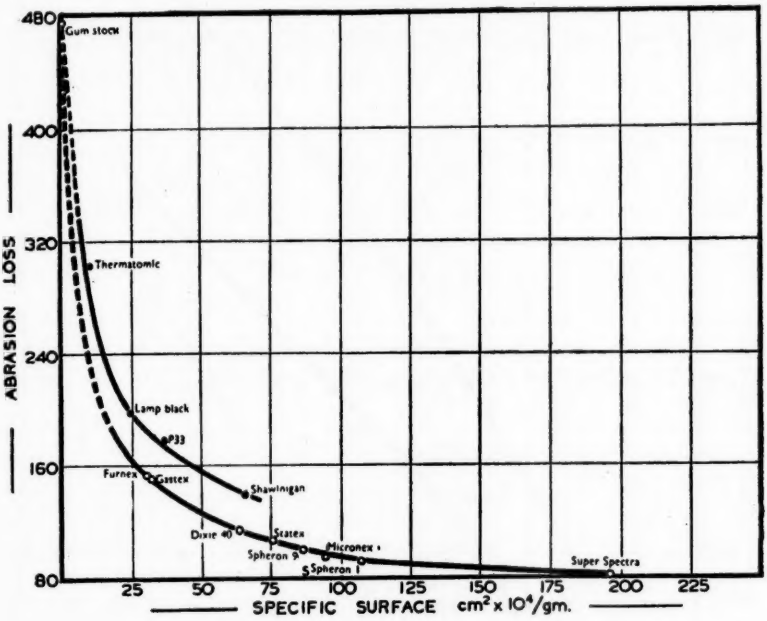

FIG. 14

in drawing the best curve through them is considered to be small. The curves show a general tendency for the minimum abrasion loss (maximum abrasion resistance) to occur at higher concentrations as the particle size increases, but in no case do they show that any particular carbon can be made equal in its effect on abrasion to a somewhat finer carbon by increasing the carbon concentration. This is a point of practical importance since, if true, it disposes of the claim sometimes made that coarse channel blacks can be made equal in their effects to finer blacks by increasing the black loading. On the other hand there is much to be said in favor of the use of larger volumes of coarser blacks in these days of rubber shortage. In this respect Statex, which gives maximum abrasion resistance at loadings of 60 to 70 per cent by weight of black on the rubber, is of particular interest. At such concentrations this carbon seems to compare favorably with coarse impingement blacks at the same concentration.

In Figures 14 and 15, minimum abrasion loss is plotted against specific surface and particle diameter. Figure 16 relates maximum abrasion resistance (reciprocal of abrasion loss) to specific surface. These curves definitely separate the carbons into two series of which one consists of Thermatomic, P-33, Shawinigan and lamp black. These four carbons give poorer abrasion re-

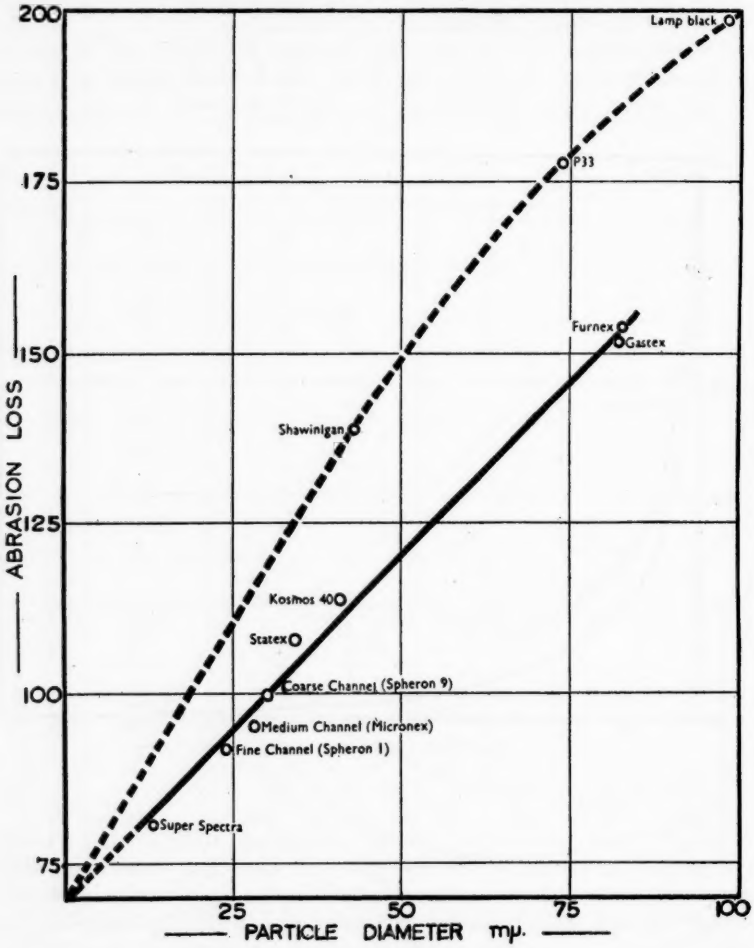

FIG. 15

sistance for a given particle size than do the other carbons. It is interesting to find the soft (thermal) blacks lining up in this way with the hard blacks. It is probable, as is shown below, that they do so for a different reason, and that the fact that the points lie on a single curve is a coincidence. The other carbons seem to vary in their effect on abrasion resistance in a regular manner with respect to particle diameter and specific surface. The points lie so nearly on the curves that it would seem that the errors of particle size and abrasion measurements have to some extent cancelled each other out. There seems

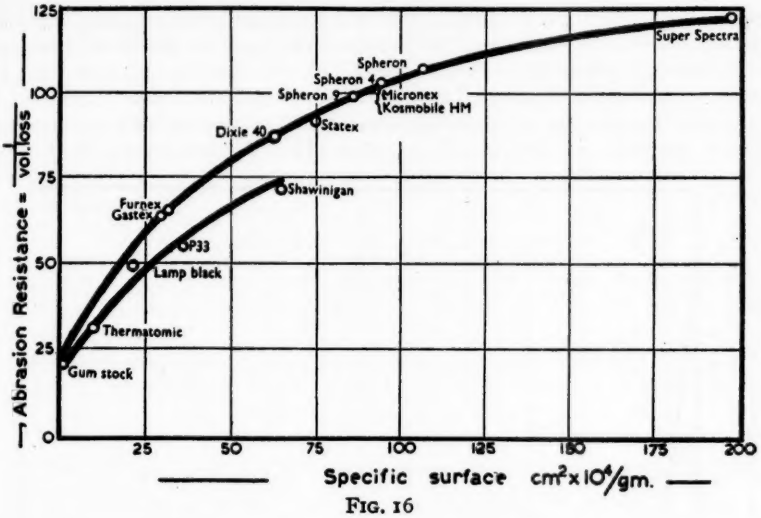

FIG. 16

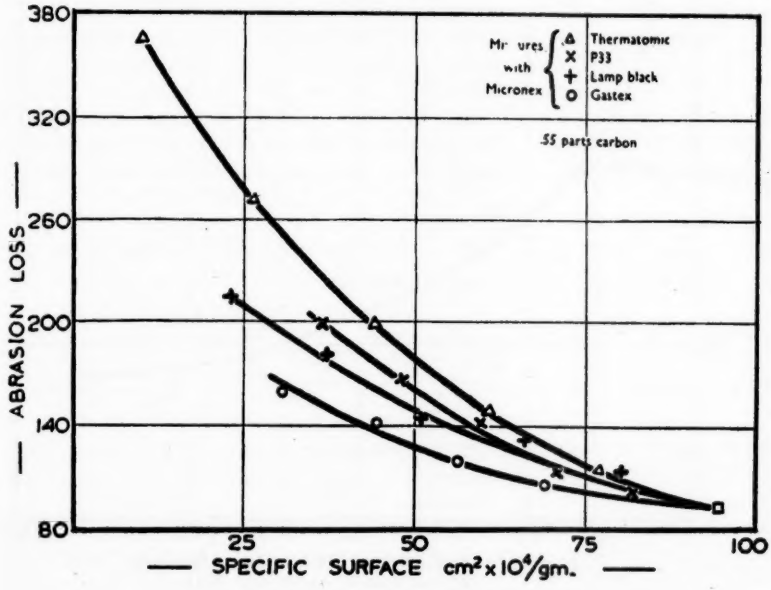

FIG. 17

little doubt, however, that these carbons form a single series giving equivalent reënforcing value. In fact it would appear from Figure 15 that the relationship of abrasion loss to particle diameter in this series of blacks between the limits of particle size represented in a linear one. If this be true and the lower curve of Figure 15 be produced to the point of infinitely small particle diameter, it meets the abrasion loss axis at a value of 70. Obviously the law breaks down before this point is reached, the figure of 70 being rather lower than seems

theoretically possible. This means that with present compounding technique the limits of abrasion resistance are reached at about 40 per cent superiority over present-day high-grade tread stocks. No doubt the practical limit is lower than this unless mixing and processing technique can be improved.

Abrasion loss-specific surface curves are drawn in Figure 17 for compounds containing mixtures of Thermatomic, lamp black, Gastex and P-33 with gas

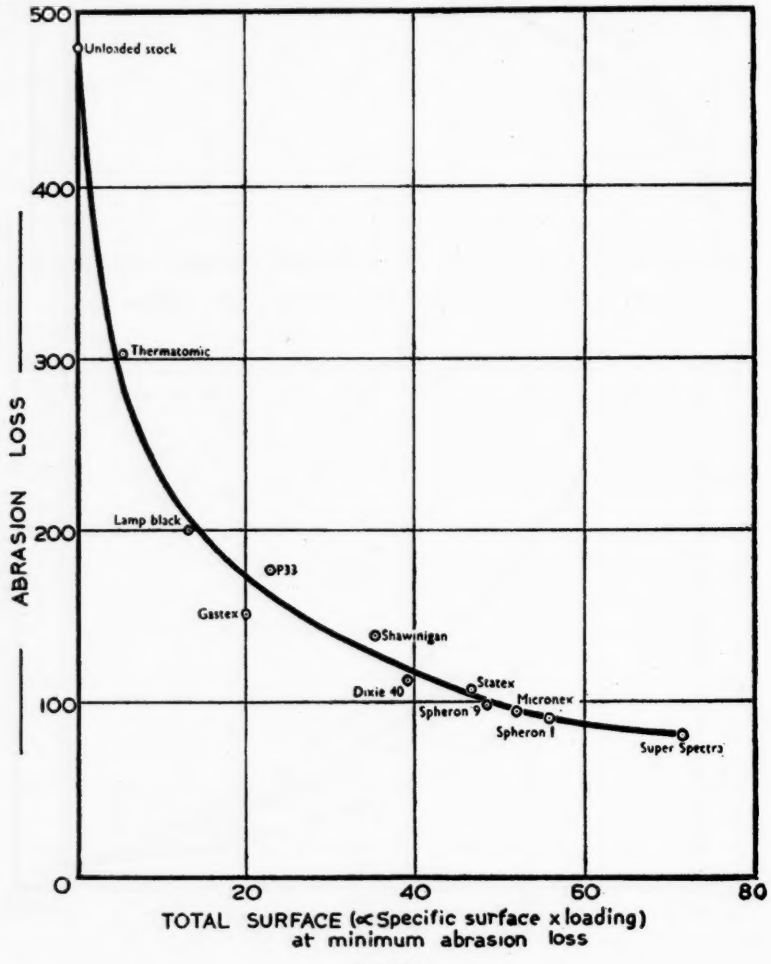

FIG. 18

black (Micronex) at a total loading of 55 per cent carbon. These curves show clearly that the abrasion loss at constant specific surface depends on the carbon, mixtures of Thermatomic and channel black giving the highest abrasion loss, and mixtures of Gastex and channel black the lowest abrasion loss at the same specific surface. These data confirm those of the tests on single blacks that lamp black and the thermal carbons promote lower abrasion resistance than would be expected from their specific surface, but they go one

step farther in indicating that the poorest black of all from this point of view is also the coarsest. This question is further considered on a later page.

Figure 18 illustrates the relationship between abrasion loss and the total surface area developed between rubber and carbon, assuming complete dispersion at the concentration giving maximum abrasion resistance. Total surface area is the product of specific surface and carbon loading. One curve can be drawn approximately through the points, the significance of which will be considered later.

DIFFERENT CLASSES OF CARBON BLACK

The data which have been presented in this paper confirm the general principle, which has been provisionally accepted by most authorities, that fineness of division is the dominant property of carbon blacks influencing their reënforcing action in rubber. These data, however, indicate that other properties of the carbon particles, or rather of the carbon-rubber system, play a part in modifying the effects of particle size and specific surface.

The properties (of rubber) which have been studied in the present investigation are tensile strength, stiffness (modulus), hardness, tear resistance, rebound resilience and abrasion resistance, and it has been shown that where a particular carbon departs from its expected position on a curve relating some property to particle diameter (or specific surface) its position with respect to the curve depends on the property. Thus, although lamp and acetylene blacks fall on one side and P-33 and Thermatomic black fall on the other side of the normal curves relating stiffness and hardness to specific surface (Figures 3 and 4), these four blacks fall on the same side (and themselves form a smooth curve) of the main abrasion-specific surface curves (Figures 14 and 16).

The carbon blacks studied in this investigation include types made from several different processes and from three different raw materials. In respect to the way in which their specific surface relates to properties in rubber they seem to fall into four classes as under:

(1) Furnace blacks (Furnex and Gastex), Kosmos (Dixie)-40, Statex, rubber-grade impingement blacks.
(2) Thermal blacks, including Thermatomic (coarse) and P-33 (fine).
(3) Lamp and acetylene (Shawinigan) blacks.
(4) Color-grade impingement blacks, of which Super-Spectra is the only one included in the present study.

The carbons in class (1) produce in relation to their fineness of division compounds of normal stiffness and hardness, normal to high resilience, normal tensile strength and normal abrasion resistance.

Those of class (2) give soft and stretchy vulcanizates of normal resilience, normal tensile strength and low abrasion resistance.

Class (3) comprises carbons giving hard and stiff compounds of relatively low tensile strength, low resilience and low abrasion resistance.

Class (4) judged by a single grade of black Super-Spectra, and considering its extreme fineness of division, gives vulcanizates of low tensile strength, normal stiffness and hardness, normal (or high) resilience and normal abrasion resistance. This class is possibly better regarded as a subclass of (1) than as a separate class.

In the formulation of the above classification, tear resistance has been left out of consideration because the test is not sensitive enough for use to be made of it in the separation of the carbons into different groups.

CARBON SURFACE AND REËNFORCEMENT

From a consideration of the properties which have been studied above and within each carbon class as here defined the following conclusions emerge: (1) tensile strength and tear resistance increase with increasing surface up to about one million sq. cm. per gram and then diminish; (2) stiffness (modulus) increases slightly but probably continuously with increasing surface; (3) B.S.I. hardness increases continuously with increasing surface; (4) resilience decreases continuously with increasing surface, and (5) abrasion resistance increases continuously with increasing surface.

It will be argued below that of the above properties, one only, abrasion resistance, can be regarded as a criterion of reënforcement.

Reënforcement, although a somewhat nebulous term which has been used in different senses by different authors, is generally agreed to imply improvement in properties of vulcanized rubber brought about by the incorporation in it of finely divided fillers. Now substantial improvement in properties such as tensile strength and tear resistance can be attained by other means. High tensile strength, for example, can be produced in noncarbon black stocks by the use of certain accelerators or by certain latex processes. Such stocks are not considered to be reënforced because they do not contain reënforcing fillers, and more particularly because they have little value in resisting abrasive wear.

Vulcanizates with high tensile strengths have often high tearing resistance, as in the case of pneumatic tread stocks, but sometimes, *e.g.*, where accelerators are employed which produce high tensile in unloaded stocks, the tear resistance is low. Exceptionally high tearing resistance can, however, be produced in nonblack stocks by certain latex processes. The abrasion resistance of such compounds is poor.

Hardness and stiffness are properties which have no necessary relation to reënforcement. Lamp-black loaded stocks, for instance, are stiffer than channel black stocks having the same carbon concentration, but have considerably poorer tensile strength, tearing resistance and abrasion resistance. Hardness and stiffness continue to increase with increasing black concentration, and in this respect differ from tensile strength, tearing and abrasion resistance, which pass through an optimum value and then decrease.

Rebound resilience diminishes continuously with increased carbon concentration. Up to a point, therefore, it decreases as tensile strength, tearing and abrasion resistance increase, and hence high reënforcement is accompanied by low resilience (an undesirable property). Resilience, however, like hardness and stiffness, is not a reënforcing property, as it does not pass through a minimum value corresponding to the minimum abrasion loss but continues to decrease with increased loading. Low resilience, moreover, can be produced in compounds having little or no reënforcing value.

Of the different properties considered, high abrasion resistance alone seems to depend on the addition of reënforcing carbons to the rubber compound. In fact there appears to be no other known technique which will achieve this object. Probably the most reliable assessment of the resistance to abrasive wear is that which compares the rate of wear of pneumatic treads which have been run on the road. It is, therefore, suggested that a type of abrasion machine which correlates with road testing when differences of a few per cent only between the compounds under comparison are involved provides the best means of assessing reënforcement.

Although none of the above properties taken singly (except abrasion resistance) can be regarded as a measure of reënforcement, the energy absorbed when a rubber vulcanizate is stressed to rupture gives an indication of its reenforcing properties. This work of extension or proof resilience[10] is represented by the area enclosed between the stress-strain curve and the elongation axis. Maximum proof resilience, except in the case of Super-Spectra compounds, shows a rough correlation with maximum abrasion resistance, as is indicated in Figure 19. The probable parallelism between energy of rupture

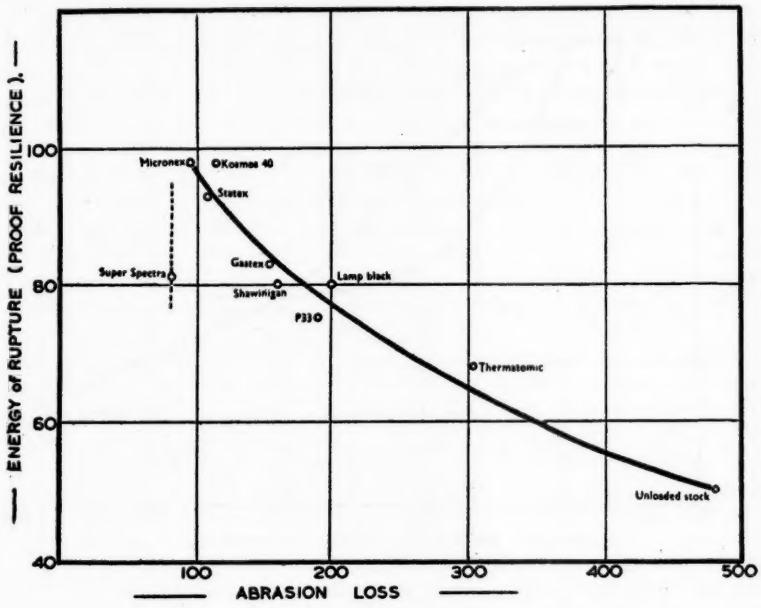

FIG. 19

and abrasion resistance was suggested on theoretical grounds by Wiegand as long ago as 1920. It seems unlikely, however, that energy determinations by means of stress-strain diagrams can be made with sufficient accuracy to distinguish between different rubber grade channel blacks.

Wiegand and Ladd[2] state that the product of energy of rupture and Shore hardness "is regarded by some as the best criterion of abrasion resistance or road wear. Energy of rupture measures overall reënforcement. Shore hardness determines the freedom from excessive crawl or squirm which appears to be *sine qua non* of maximum road wear."

In Figure 20, the product of energy of rupture and the reciprocal of the B.S.I. hardness number (which is a more accurate measure of hardness than Shore durometer) is related to abrasion loss. The curves show that such a method of assessing abrasion loss gives values far too high for lamp and acetylene blacks. It also brings the coarse and fine thermal blacks too close together, and shows too big a gap between the impingement blacks and Statex.

The question now arises as to whether specific surface is the dominant factor affecting reënforcement (which is regarded here as synonymous with abrasion resistance), or whether some other factor dependent on diameter is

dominant. As the particles are spherical (or spheroidal), the ratio of surface to diameter is constant for all particles and to that extent reënforcement may be said to depend on specific surface within each of the two carbon series as indicated in Figures 14 and 16. It has further been shown (Figure 18) that if total surface area in contrast to specific surface at optimum loading for abrasion is plotted against minimum abrasion loss, the two series come closer

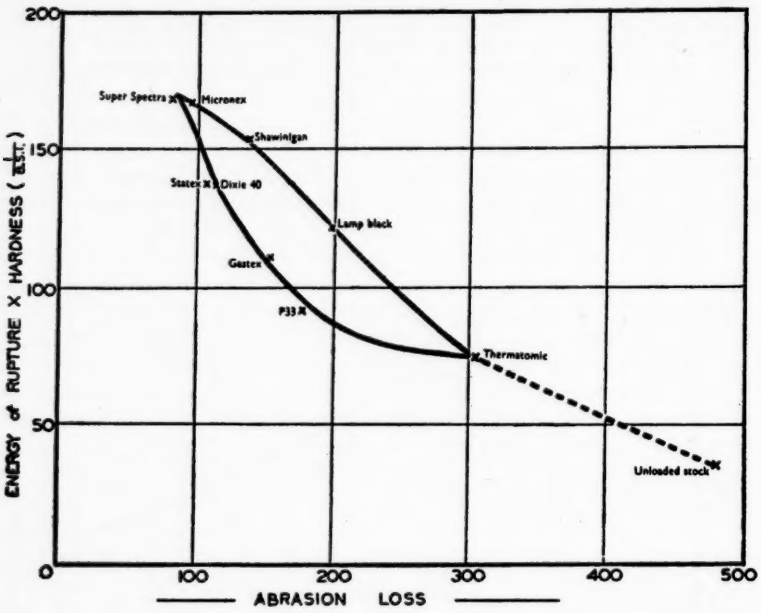

FIG. 20

together, and throughout the whole range of carbons, with the exception of Gastex and P-33, all are ranged in order of surface area. This suggests that the total extent of surface between rubber and carbon filler, which depends on the product of specific surface and carbon concentration, is the primary reenforcing factor. But such a hypothesis raises difficulties of which only one need be considered here. At concentrations beyond the abrasion optimum, unless the effective dispersion of the carbon particles declines, the surface area between rubber and filler is increasing as reënforcement is decreasing. The indications are that dispersion of carbon continues to loadings considerably beyond those for maximum abrasion resistance. It is difficult, for example, to account for the linear decrease in resilience with carbon loading, unless it be assumed that the dispersion of carbon is equally effective at all concentrations. There are other reasons for this view, and it would therefore appear that, although surface as such cannot be divorced from the phenomena of reënforcement, total surface in itself does not explain it.

HYSTERESIS AND DISPERSION

A consideration of the fundamental principles involved in the production of hysteresis is outside the scope of the present paper, which merely calls attention to certain aspects of the problem insofar as it is related to reënforce-

ment. Hysteresis is a phenomenon which occurs in unreënforced as well as reënforced compounds. In most, if not all, types of mixing in which the rubber phase is considerably diluted, that part of the hysteresis due to the rubber itself, *i.e.*, the rubber-sulfur-accelerator complex, is subordinate to that resulting from dilution. Thus a vulcanizate having a concentration of 55 parts by weight impingement black to 100 parts rubber has a rebound resilience value of 65 per cent, compared with 93 per cent possessed by the unloaded stock (Figure 7). This means that about four-fifths of the hysteresis, *i.e.*, deficiency of resilience, is caused by the incorporation of carbon in the stock. Dilution of the rubber phase by means of hibad or vibad extenders provides an example of hysteresis not accompanying reënforcement in which volume for volume the greater part of the hysteresis is due to the nonrubber part of the mixing.

It seems to follow from the two examples quoted above that, whatever the ultimate cause of hysteresis, the frictional effects involved are, in part at least, different in different types of compound. In the case of carbon reënforced rubber stocks, much of the hysteresis appears to result from frictional effects between particles of undispersed carbon. Such a view receives some support from the facts considered below.

The electron microscope has confirmed what was previously suspected, that those carbons which produce the hardest vulcanizates commensurate with their particle size, *i.e.*, lamp and acetylene, and which, as shown in this paper and by Wiegand, are anomalous in other respects, tend to flocculate in chain-like structures, and there are reasons for the belief that such structures are still in evidence when those particular carbons are present in vulcanized rubber. One reason is the lower resilience imparted to the rubber than is expected from particle size considerations, such decreased resilience apparently resulting from incomplete dispersion of the carbon particles. Another reason is the relatively high electrical conductance of lamp and Shawinigan blacks, a condition which can hardly arise unless the particles are in some degree touching each other.

It is known that the resilience of vulcanizates loaded with impingement black can be increased considerably by certain processes, such as heat treatment of the unvulcanized stock. This increased resilience, which accompanies an increase in electrical resistivity, has been attributed to a rearrangement of the carbon particles from a state of partial flocculation to one of more complete dispersion[7]. This again suggests that the more complete the dispersion the higher is the resilience.

It is interesting to speculate on the possibilities of recovering the resilience which has been lost as a result of carbon incorporation in the stock. A compound having a concentration of 50 parts of channel black by weight per 100 parts of rubber has a rebound value of 50° C, about 28 per cent lower than that of the unloaded stock. Such a compound, if heat-treated in the approved manner before vulcanization, will have a rebound value as much as seven or eight per cent higher than it would have had if unheated. In other words the heat treatment has regained about one-quarter of its original loss in resilience caused by black incorporation, and it has accomplished this by a rearrangement of carbon particles resulting in a more complete state of dispersion. To what extent, if any, the remaining 75 per cent of the lost resilience can be recovered by suitable treatment of the uncured stock or by improved methods of black incorporation, only further research will decide.

Of the undispersed material, it may well be that a substantial proportion exists in the form of more or less compact aggregates or from a few to many hundreds or even thousands of particles. Such aggregates (of impingement

black) cannot be resolved in an ordinary optical microscope unless they consist of more than about 1,000 particles, and they almost certainly are present in what appears from microscopical examination of thin sections to be a stock without any undispersed carbon.

It is tentatively suggested that carbon black exists in a vulcanized rubber compound in four different states: (1) agglomerated, comprising those particles which are present in the form of compact clusters; (2) flocculated, or forming a network of strings or chains in which individual particles are in actual contact; (3) dispersed, in which each carbon particle is separated from its neighbors but is not firmly bonded to the rubber, and (4) dispersed and linked to rubber macromolecules.

ANOMALIES

In each property which has been studied during the present investigation, the following carbons have formed a single series varying progressively with particle size: furnace carbons (including Gastex and Furnex), Kosmos-40, Statex, rubber-grade impingement carbons. This series, or class as it has been termed in this paper, may be regarded as the norm, other blacks being anomalous in one or more properties with respect to fineness of division. Super-Spectra seems to fall in the normal carbon black class in its effects on rebound resilience and abrasion resistance, but it has been placed tentatively in a separate class because it imparts poorer tensile and tearing properties than is expected from its particle size. To obtain further information on this point, more work is needed on compounds covering the range 13 to 24 mμ.

It is important that the factors modifying the effects of particle size should be understood, since any satisfactory theory of reënforcement must take account of them. Wiegand and Ladd[2] ascribe the anomalous behavior of acetylene black and lamp black "to the presence and persistence of carbon to carbon complexes or networks which impede by competition the reënforcing action." It seems probable that the complete explanation will be based on some such hypothesis as this.

The above authors further suggest that the subnormal properties of the thermal carbons are "due to complete inertness; *i.e.*, total absence of carbon : carbon or carbon : rubber complexes". Although it appears that the coarse thermal carbons (Thermatomic) have very low reënforcing power, this is not the case with fine thermal carbon (P-33). The abrasion resistance given by P-33 is actually rather better than that promoted by lamp black, although in relation to its smaller particle diameter P-33 is not quite equal to lamp black. It is, however, both actually and relatively better than Thermatomic, as is brought out in Figure 17, which depicts abrasion loss-specific surface curves of mixtures of blacks. These curves show clearly that along the lines of constant specific surface there is a progressive increase in abrasion loss from Gastex through lamp black and P-33 to thermatomic. If the reënforcing effect of P-33 were relatively no better than that of Thermatomic, all the points representing the different proportions of the mixture of gas black and P-33 would lie (or theoretically ought to lie) on the Thermatomic-gas black curve. This argument assumes a concentration of 55 per cent carbon to be reasonably near the optimum for each carbon, and Figure 13 shows such an assumption to be justified.

It would, therefore, seem that in the case of the fine thermal blacks there is little justification for the view that carbon-rubber structures are not formed. It is suggested here that such structures are built up, but that the bond be-

tween rubber and carbon is weaker than it is in the case of the socalled semi-reënforcing (Gastex) and fully reënforcing carbons. This view receives some support from a consideration of the surface activity of P-33 black, which is shown by adsorption measurements to be low compared to its extent of surface[11].

THE MECHANISM OF REËNFORCEMENT

It has been argued in the present paper that, although fineness of division is the primary factor governing reënforcement, the concept that this is solely the result of the extent of surface developed between carbon and rubber is unsatisfactory in that it leads to the illogical conclusion that, as surface increases, reënforcement, though at first increasing, later decreases. A satisfactory theory must, therefore, reconcile this apparent contradiction.

Any theory of reënforcement seems to demand the existence of some kind of bond between rubber and individual particles of dispersed carbon. A possible means of attacking the problem is based on the hypothesis that only a proportion, probably not large, of the dispersed carbon is concerned with reenforcement. This is the carbon in condition (4) above, which is assumed to be bonded to the rubber macromolecules. On such a view the number of carbon particles in this condition would increase more or less uniformly in the early stages of loading, but the rate of increase of bonded carbon would decline towards the optimum reënforcing point, saturation being reached at maximum abrasion resistance. The part played by hysteresis of such rubber-carbon structures would be, compared with that resulting from the unbound carbon, a comparatively small one. The number of such rubber-carbon complexes formed would increase with decreasing particle size because of the greater number of particles available, with a concomitant increase in the degree of reënforcement. With the exception of the thermal carbons, there would seem no need to postulate an increased strength of bond as the particles decrease in diameter.

Either on the above or on other hypotheses it would appear that the strength of attachment to the rubber molecules of the individual particles of fine thermal carbon is weaker than that of the others with the exception of that of coarse thermal carbon, which is the weakest of all. The weaker bond of the thermal carbons may be in part a consequence of decreased surface activity, but this raises the question of the nature of the forces operating between carbon and rubber, and involves a consideration of the structure of the rubber molecule. These questions are outside the scope of the present paper.

No attempt is made in this paper to propound a theory of reënforcement, and the above tentative suggestions are brought forward merely as a basis for discussion and further work. It is recognized that there are other angles from which the problem might be approached. Space does not permit of the discussion of existing theories of reënforcement.

SUMMARY AND CONCLUSIONS

Carbon blacks can be grouped into different classes according to the way in which their fineness of division relates to different properties in rubber. Within any one class the principal properties vary in a regular manner with particle size. The normal class consists of the furnace carbons, Kosmos (Dixie)-40, Statex, the rubber-grade impingement carbons, and possibly, the color-grade impingement carbons. The subnormal classes consist of thermal carbons and acetylene and lamp blacks.

Irrespective of the above classification, the properties which depend more on fineness of division than on other factors are rebound resilience, abrasion resistance, tensile strength and tear resistance. The lower limit of particle diameter for best tensile strength and tear resistance appears to be higher than that for abrasion resistance. B.S.I. hardness and electrical conductivity are properties which depend at least as much on other factors as on particle size. Stiffness (modulus) depends more on other factors than on particle size. Factors modifying the effects of particle size (or specific surface) include the presence of carbon-carbon structures and a reduction in strength of bond in rubber-carbon structures.

Carbon black is thought to exist in rubber in four states: agglomerated, flocculated, dispersed, and bonded to the rubber molecules (the reënforcing fraction). Abrasion resistance is regarded as providing the only reliable measure of reënforcement.

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REFERENCES

[1] Wiegand, *Can. Chem. & Process Inds.* **25**, 579 (1941); *India Rubber World* **150**, 270 (1941).
[2] Wiegand and Ladd, *Rubber Age* (N. Y.) **50**, 431 (1942).
[3] "Columbian Colloidal Carbons", **1942**, p. 3.
[4] Tidmus and Parkinson, *Trans. Inst. Rubber Ind.* **13**, 52 (1937).
[5] To be published in *Trans. Inst. Rubber Ind.*
[6] Gough and Parkinson, *Trans. Inst. Rubber Ind.* **17**, 168 (1942).
[7] Parkinson, *Trans. Inst. Rubber Inst.* **16**, 87 (1940).
[8] To be published in a forthcoming paper.
[9] Lambourn, *Trans. Inst. Rubber Ind.* **4**, 210 (1928).
[10] "Columbian Colloidal Carbons", **1938**, p. 77, and earlier papers.
[11] "Columbian Colloidal Carbons", **1942**, p. 23.

STABILITY OF BUTADIENE

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The urgency for the expansion of synthetic rubber production involves a number of problems, not the least of which are the storage and handling of the hydrocarbon raw materials. Although butadiene possesses a certain degree of instability, the goal of this investigation was to obtain more detailed insight into the chemical reactions occurring during storage and handling. This information will permit a more intelligent selection of the conditions under which the diolefin can be handled or stored safely and with a minimum loss of valuable material.

From a broad point of view, butadiene can be considered unstable from two aspects: (1) With respect to its elements; that is, butadiene reverts to its elements, carbon and hydrogen, under an effective impulse and appropriate conditions, and results in the evolution of considerable heat:

$$C_4H_6 \rightarrow 4C + 3H_2 + \text{approx. } 27{,}000 \text{ cal.}$$

At least one report[1] states that this reversion apparently took place under high hydrostatic pressure.

(2) Polymers are also formed with the evolution of heat:

$$nC_4H_6 \rightarrow (C_4H_6)_n + \text{approx. } n\ 19{,}000 \text{ cal.}$$

Thus the lower conjugated dienes, in general, can be considered as compounds existing at a high level of chemical energy with a tendency to drop to lower levels, on the one hand, by decomposition to elements and, on the other, by polymerization. Under conditions affording poor dissipation of heat, these reactions can produce high localized temperatures and thus spontaneously proceed with extreme rapidity, since they have positive temperature coefficients.

Another type of instability results when the diolefin reacts with other available substances, such as oxygen of the air, to form peroxides which are *per se* unstable. However, polymerization is the most important degradation reaction likely to be encountered in storage and handling, and hence considerable emphasis is placed on it in this discussion.

For years it has been known that butadiene and homologous conjugated diolefins undergo spontaneous polymerization to liquid polymers even at ordinary temperatures. Higher temperatures are known to result in the formation of relatively larger quantities of the polymer. Occasionally the formation of plastic rubbery polymers has been noted. In the latter cases some substances known to act as polymerization catalysts, *e.g.*, peroxides or active metal, were generally known to be present. It has thus become clear in recent times that butadiene is capable of at least two types of polymerization, which may occur separately or concurrently depending on conditions:

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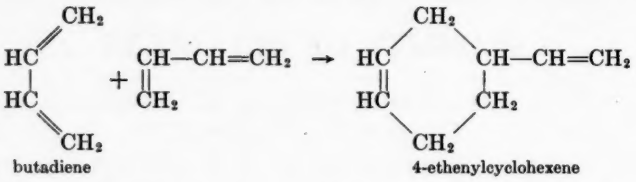
1. Cyclic polymerization or thermal dimerization results when two molecules of butadiene unite to form a ring type compound by Diels-Alder condensation:



The resulting dimer of butadiene is a stable liquid boiling at 127° C and possessing a characteristic odor. It is miscible with butadiene in all proportions at ordinary temperatures and does not tend to undergo further polymerization to any major extent, although a slow trimerization reaction (combination of one molecule of dimer and one of monomer) has been noted[2].

2. Chain polymerization results in the formation of high-molecular-weight hydrocarbon material varying in consistency from a tacky fluid to a rubbery mass, and in certain instances to a resinous solid, depending on conditions. It is generally believed that this type of polymer results from the union of butadiene molecules in long chains, such as:

$$n CH_2{=}CH{-}CH{=}CH_2 \rightarrow \cdots{-}CH_2{-}CH{=}CH{-}CH_2{-}CH_2{-}CH{=}CH{-}CH_2{-}\cdots$$

There is evidence that some butadiene molecules are included in the chain by 1, 2 addition, whereby unsaturated branches are produced.

The higher-molecular-weight polymers of this type are sometimes insoluble and tend to separate from the liquid monomer. It is believed that resinous properties and insolubility result from cross-linking between polymer chains.

In the present investigation an endeavor was made to study these two types of polymerization independently and to determine the effects of variables, such as temperature, catalysts, extent of surface, and type of surface.

THERMAL POLYMERIZATION

The rate of conversion of butadiene and other conjugated dienes to their respective dimers was studied in the gas phase by Kistiakowsky and Ransom[2]. A brief study of the rate in the liquid phase was made by Lebedev *et al.*[3], but only at somewhat elevated temperatures. No systematic investigation under commercial storage, handling, and distillation conditions has been made, to the authors' knowledge.

Several experiments were carried out in which liquid butadiene was sealed in tubes of steel or glass and maintained at a given temperature for a known length of time. Ultimately the tubes were opened and analyzed for the presence of polymer. The results of some of these experiments are presented in Table I.

The tests in steel bombs were made on freshly distilled (in a fifty-plate Stedman column), 97–99 per cent pure diolefin derived from the cracking of petroleum. The main impurity was 1-butene. The α-acetylene content was not more than 0.05–0.1 per cent. Although care was taken to exclude air while filling the steel bombs, some contact occurred during the distillation. Extreme precautions to eliminate oxygen were taken with the samples sealed in glass. Materials were handled under vacuum or in a sealed glass system filled with deoxygenated nitrogen. The technique was similar to that of

Medvedev *et al.*[4] in their recent study of the polymerization of chloroprene. The apparatus used for filling the glass ampoules consisted of a small column from which a sample in contact with pyrogallol was distilled into a flask connected to a reflux condenser. Here the sample was allowed to reflux for about 30 minutes before it was drawn into the evacuated ampoule. The sample was then frozen with liquid nitrogen and the ampoule sealed with a torch. The sealed ampoule was placed in a constant-temperature bath for a definite time.

TABLE I

THERMAL POLYMERIZATION OF BUTADIENE

Expt. No.	Temperature (° C)	Temperature (° F)	Composition of sample	% Hydroquinone added	Time (hrs.)	Wt. % Polymerized: Solid	Wt. % Polymerized: Liquid	% Polymerized per hr.: Found	% Polymerized per hr.: Calcd.
			Mild steel reaction tubes						
1	82	180	Pure C_4H_6	None	93	3.8	6.7	0.112	0.15
2	82	180	Same	0.05	93	0.2	6.8	0.075	0.15
3	60	140	Same	None	168	0.5	2.0	0.015	0.014
4	60	140	Same	0.05	168	0.2	1.9	0.013	0.014
5	121	250	25% C_4H_6, 54% *n*-C_4H_8, 19% iso-C_4H_8	None	0.5	0.66		1.32	0.85
6	121	250	Same	None	1.0	0.71		0.71	0.85
7	121	250	Same	None	1.5	1.01		0.67	0.85
			Glass reaction tubes						
8	60	140	Pure C_4H_6	None	162.5	2.43		0.016	0.014
9	45	113	Same	None	790	1.72		0.0022	0.0025
10	30	86	Same	None	41.5	0.03		0.0007	0.0004

Polymer was determined in the sample, after removal from the bath, by opening the ampoule, allowing the unreacted butadiene to boil off under room conditions, and weighing the polymer left behind. In some cases precipitated solid polymer was separated first. To make certain that no dimer was carried over with the vapors, the butadiene was recondensed and distilled in a small fractionating column in the presence of a small amount of added isoöctane to act as carrier. The amount of dimer could then be determined by the refractive index of the isoöctane-dimer mixture left as the residue in the fractionating column. No appreciable amount of dimer was found in this portion. In most of the experiments dimer was produced in too small a quantity to allow satisfactory characterization. However, in experiments where conversion was permitted to proceed to considerable percentages, a product was formed at least 95 per cent of which distilled at 127° C.

A number of important conclusions can be drawn from Table I. For example, the temperature coefficient of the polymerization reaction is quite high (Figure 1). The plotted points fall nearly on a straight line, and the lower portion of this line is practically identical with a calculated curve. This curve was obtained by substituting liquid-phase concentration in the equation of Kistiakowsky and Ransom[2] for the vapor-phase dimerization reaction. The dimerization of butadiene in the vapor phase is a rather clean-cut bimolecular reaction, the rate of which can be expressed by the equation:

$$\text{rate (moles cc.}^{-1}\text{ sec.}^{-1}) = 9.20 \times 10^9 \exp.\ (-23{,}690/RT)\ [C_4H_6]^2$$

Barring the first run in Table I, the amount of solid polymer produced was insignificant, and the remarkable agreement between the observed rates of

dimerization (liquid polymer formation) and those calculated by substitution of liquid-phase concentrations in the equation can be seen in the last two columns. The calculated rates of dimerization in the vapor phase under these conditions are negligible.

Deviation of the experimental data from the calculated curve in Figure 1 is greater at higher temperatures. This is probably due to the greater con-

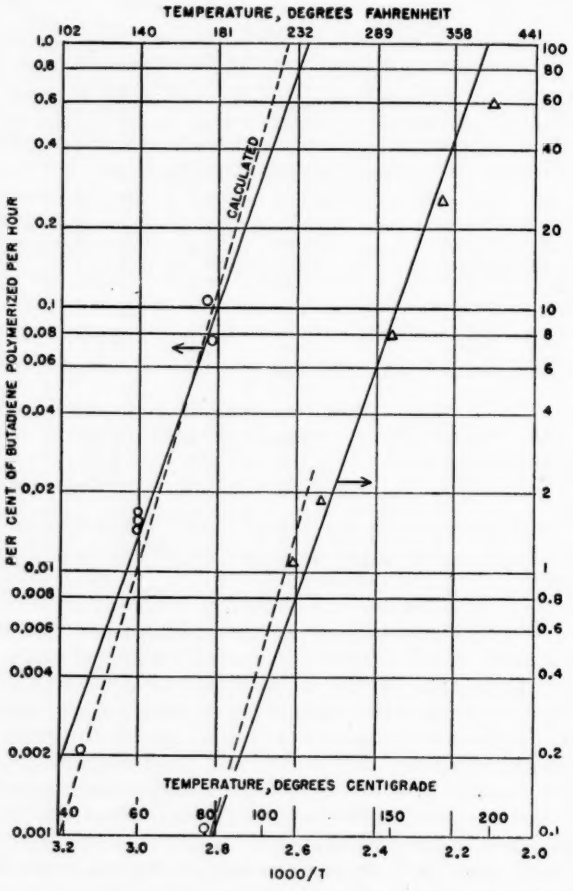


FIG. 1.—Rate of dimerization of pure butadiene in liquid phase as a function of temperature. ○ = this investigation; △ = Lebedev et al[3].

versions to which the reactions were permitted to proceed in Lebedev's work. Adherence to a linear plot of log rate against $1/T$ in Figure 1 would be expected only when the concentration of monomer remains virtually constant. Deviation is, therefore, observed as appreciable amounts of polymer product dilute the monomer.

A further point of interest is that the data for runs in various types of vessels fall on the same curve, indicating that the types of surface studied have no pronounced catalytic influence on the dimerization reaction.

Actually, the dimerization reaction was not the only type of polymerization in some of the runs. In experiments 1 to 4 (Table I), various amounts of a solid (rubbery) polymer were also obtained. However, the separation between the solid and liquid could not be made strictly quantitative because of the gellike form of the solid; consequently the apparent proportion of solid polymer is probably somewhat high. In experiments 1 and 3, and 2 and 4, tests were made both in the absence and in the presence of the antioxidant, hydroquinone, at two different temperatures. Butadiene from the same distillation was used in these comparisons. Even casual inspection of the resulting data reveals that the presence of the antioxidant inhibits the formation of plastic polymer but has no appreciable effect on the rate of formation of dimer. In fact, so far as the authors know, no way has as yet been found for minimizing the dimerization reaction in concentrated butadiene other than the use of the lowest practical storage and handling temperatures.

TABLE II

POLYMERIZATION OF BUTADIENE IN PRESENCE OF PEROXIDES[a]

Expt. No.	Temperature (° C)	Temperature (° F)	Peroxide added	Active O (P.P.M.)	Time (hrs.)	Wt. % Polymerized	% Polymerized per hr.
10	30	86	None	0	41.5	0.03	0.0007
11			Benzoyl	13	19.5	0.015	0.0008
12			Benzoyl	330	19.5	0.11	0.0056
13			Benzoyl	1275	20.5	0.10	0.0049
9	45	113	None	0	790	1.72	0.0022
14			Benzoyl	13	24	0.118	0.0049
15			Benzoyl	13	788	4.38	0.0055
16			Tetralin	20	788	5.29	0.0067
17			Benzoyl	500	24	0.432	0.0180
18			Benzoyl	1275	24	0.81	0.034
19			Benzoyl	1290	783	26.98	0.0342
20			Tetralin	2000	788	30.0	0.0381
8	60	140	None	0	162.5	2.43	0.016
21			Benzoyl	13	162.5	4.89	0.030
22			Tetralin	20	162.5	4.21	0.026
23			Benzoyl	1155	162.5	34.49	0.212
24			Tetralin	2000	162.5	25.52	0.157
25			Benzoyl[b]	1290	162.5	8.32	0.0512
26			Tetralin[b]	2000	162.5	26.83	0.165
27			Benzoyl[c]	1290	162.5	10.68	0.0657
28			Tetralin[c]	2000	162.5	27.91	0.172
29	45	113	Peroxidation by air	49[d]	720	2.70	0.0038
30			Same	193[d]	720	5.75	0.0079
31	60	140	Same	60[d]	264	6.4	0.024
32			Same	171[d]	264	8.1	0.031

[a] 98–99% butadiene in sealed glass tubes.
[b] In presence of steel strips.
[c] In presence of glass beads.
[d] Determined by the ferrous thiocyanate colorimetric method[5].

It is not possible to state definitely at this time that the truly thermal reaction does not give rise to some plastic polymer, although it is certain that such material is produced only in very small amounts. This uncertainty is due to the difficulty in experimentally removing the last traces of peroxides from a test-sample, and hence in completely eliminating the second type of reaction discussed below.

POLYMERIZATION IN PRESENCE OF PEROXIDES

The second type of polymerization reaction which occurs in butadiene is purely peroxide-catalyzed, and is superimposed additively on the thermal reaction. The peroxide-catalyzed reaction produces largely the high-molecular-weight plastic type of polymer. Results so far available do not exclude the possibility of some dimerlike polymers also being formed in the peroxide-catalyzed reaction. Peroxide catalysts of different types were studied—benzoyl peroxide, tetraline peroxide, and peroxidized butadiene.

The results of these experiments are summarized in Table II. It is apparent that the presence of peroxide does increase the rate of polymerization of butadiene at each of the temperature levels studied. Also, with the exception of experiments 25 to 28, which will be discussed later, there is no notable difference in the effects of benzoyl peroxide and tetralin peroxide at 45° C, although a slight difference may exist at 60° C. Experiments 29 to 32, inclusive, made with the peroxide formed in butadiene on contact with air, showed considerably less activity.

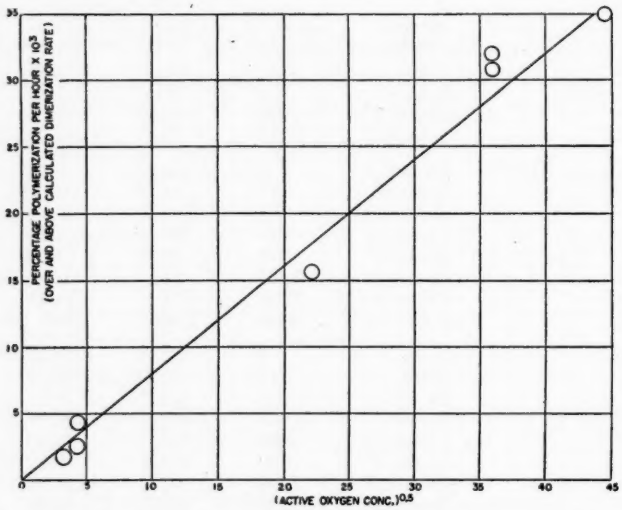


FIG. 2.—Rate of formation of high-molecular-weight polymer in pure butadiene as a function of active oxygen concentration at 45° C.

The data in Table II indicate that the rate of formation of plastic polymer is very sensitive to small amounts of active oxygen (one active oxygen atom per molecule of peroxide), but the effect becomes less pronounced as the concentration is increased. More particularly it appears that the rate of formation of high-molecular-weight polymers varies directly as the square root of the concentration of active oxygen. This is shown by a plot of the data at 45° C in Figure 2. The square-root relation has been noted in many other polymerization reactions catalyzed by peroxides. This effect is in accord with the free radical concept of polymerization catalysis.

The polymer (including dimer) in all experiments was soluble in the monomer, with the possible exception of the runs in which no peroxide was added in these some precipitation was observed.

Runs 25–28 (Table II) were made in the presence of peroxides and increased surface; in runs 25 and 26 several pieces of mild steel were present, and in runs 27 and 28 glass beads were added. This increase of surface had no effect on the rate of polymerization in the presence of tetralin peroxide, but the rate in the presence of benzoyl peroxide was decreased about 80 per cent. This may be due to deactivation or recombination of free radicals on the surface.

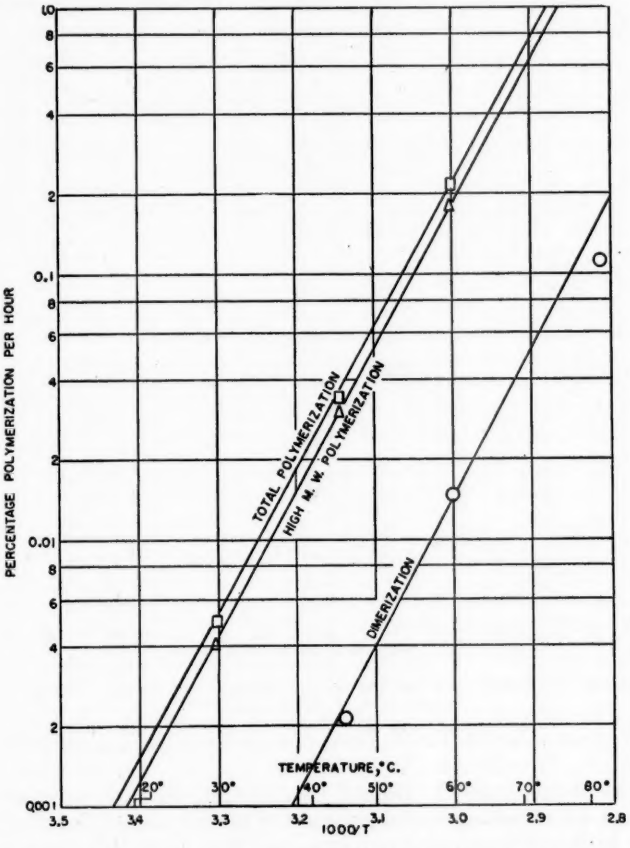


FIG. 3.—Rates of conversion of pure butadiene to dimer and to chain polymer as a function of temperature. (1200 p.p.m. active oxygen present.)

The effect of temperature on the rate of polymerization of butadiene in the presence of peroxides is shown by the conventional plot in Figure 3. The curve for the rate of dimerization in Figure 1 is shown along with the curves for the rate of polymerization to high-molecular-weight polymer in the presence of 1200 p.p.m. of active oxygen and also total polymerization (dimer plus high-molecular-weight polymer). It can be seen that, in the presence of this concentration of active oxygen, the dimerization reaction furnishes only about 10 per cent of the total polymer. The fact that all the curves have nearly the same slope indicates that the energies of activation of chain and cyclic polymerization of butadiene are practically identical.

A complete summary of the data obtained is presented in conveniently usable form in Figure 4. The data obtained in the absence of any significant amount of peroxides are plotted along the ordinate at 1 p.p.m. active oxygen, and they appear to fall quite well on the extrapolated curves for each temperature. Plotting these data at 1 p.p.m. may be justified on the grounds that this is about the minimum concentration which can be maintained with certainty in butadiene, even with the most careful technique.

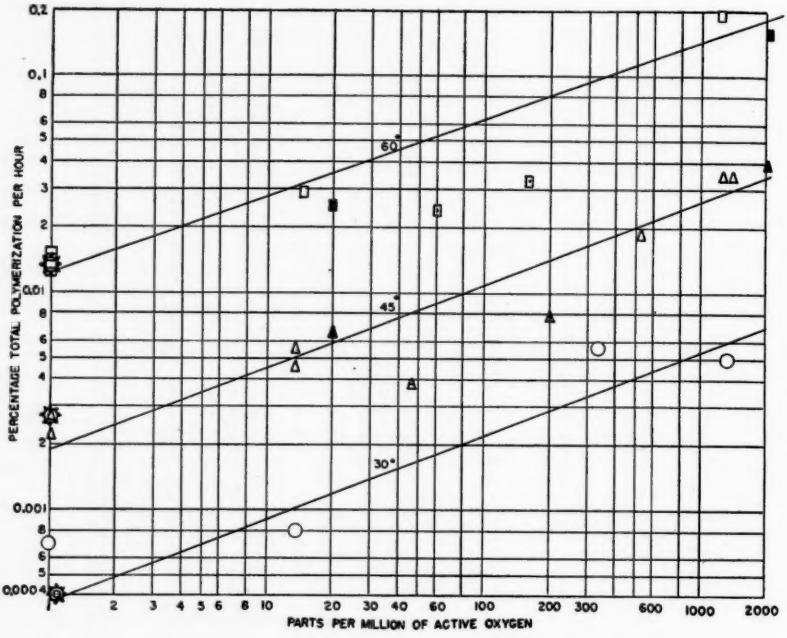


FIG. 4.—Rate of polymerization of pure butadiene as a function of active oxygen concentration at various temperatures.

□, △, ○ = benzoyl peroxide; ■, ▲ = Tetralin peroxide; ⊡, ◬ = butadiene peroxide. Starred points at extreme left are calculated from dimerization rate equation.

The data of runs 2 and 4 (Table I) demonstrate that the peroxide-catalyzed reaction can be effectively subdued by the proper use of polymerization inhibitors. It should be emphasized, however, that no inhibitor can be expected to last indefinitely. For this reason, the periodic checking of the inhibitor content of stored butadiene appears desirable, especially under conditions affording exposure to air.

PEROXIDATION OF BUTADIENE

Since it has been shown that the presence of peroxides has considerable influence on the rate of polymerization, it is important to know whether butadiene will peroxidize in contact with oxygen, air, or other oxidizing substances. This has been answered in the affirmative.

Experiments were made in which freshly distilled butadiene was kept saturated with air at room temperature and at 50° C under pressure. These showed active oxygen concentrations of 120 and 460 p.p.m. after 48 and 24

hours, respectively. When 25 cc. of the peroxidized butadiene obtained at the end of the room temperature run were permitted to evaporate to dryness under room conditions, 0.11 gram of an oily substance, having a sharp aldehydic odor and an active oxygen content of 18,000 p.p.m., remained as residue.

Compounds, such as hydroquinone, pyrogallol, catechol, etc., are quite effective as inhibitors of the peroxidation of the diene. For example, 300 cc. of butadiene containing 0.1 weight per cent of hydroquinone completely resists the peroxidizing action of a stream of air, at room temperature and 50 pounds per square inch pressure, for more than 120 hours.

INSTABILITY IN DISTILLATION

From the foregoing the extent of polymerization at the elevated temperatures of distillation can be predicted with considerable certainty. However, a more hazardous form of instability may be encountered. As pointed out above, there is a tendency for peroxides to accumulate as "bottoms". Distillation in batch to low bottoms, for example, may result in active oxygen concentrations in the residue so high that further heating produces an explosive autoöxidation. The danger involved in distilling peroxidized butadiene to very low bottoms is emphasized by the following experiment: The peroxidized butadiene produced in the 50° C test was permitted to evaporate under room conditions. After all of the liquid hydrocarbon had disappeared from the flask and only a residue remained, the vessel was covered lightly and heated on a sand bath so that the temperature rose at the rate of 10° to 12° C per minute. When 125° C was reached, violent decomposition took place within the flask, the cover of the flask was displaced, and large volumes of white fumes were evolved. Further heating to 250° C resulted only in the charring of the trace of residual material. Experience indicates that the explosion hazard may be eliminated by distilling in the presence of an adequate amount of peroxide-destroying substance and preventing air from returning to the distillation vessel after the heat is removed. In the case of batch distillation of butadiene-containing materials of high peroxide content, it is desirable that the peroxides be destroyed by the antioxidant before distillation is started. Since most peroxides require appreciable time for decomposition by antioxidants, the elimination can be conveniently effected by heating under pressure until the absence of peroxides is indicated by chemical test. In distillation the addition of a hydrocarbon boiling higher than butadiene is an added factor of safety, since such a procedure limits the degree to which the peroxides can be concentrated during a single distillation.

SUMMARY

1. The most prominent polymerization of pure butadiene in the absence of peroxides is dimerization. This reaction is thermally activated, and does not appear to be catalyzed by peroxides or by steel surfaces.

2. Butadiene is also capable of independent polymerization to high-molecular-weight polymer, but in the absence of peroxides this reaction is insignificant compared to dimerization. The effect of temperature on the rates of each of these reactions has been determined.

3. In the presence of appreciable amounts of peroxides, polymerization to high-molecular-weight polymer becomes prominent, and is superimposed additively on the thermal dimerization reaction.

4. The addition of suitable antioxidant inhibits the formation of high-molecular-weight polymer, but has no appreciable effect on the rate of dimer formation.

5. The rate of high-molecular-weight polymerization is directly proportional to the square root of the concentration of peroxides (active oxygen).

6. Butadiene is readily peroxidized by air, but this peroxidation may be inhibited for a time by the presence of antioxidants.

7. The peroxides are not readily volatile, and tend to accumulate in the residue if the diene is evaporated or distilled away. Concentration beyond a certain point yields an unstable residue which may decompose with violence when heated. Precautions for distillation of such peroxidized material are given.

ACKNOWLEDGMENT

The authors wish to thank those among their colleagues, particularly M. W. Swaney and I. S. Rice, who aided with the experimental work and manuscript, also the Standard Oil Development Company for permission to publish.

REFERENCES

[1] Scott, *News Ed.* (Am. Chem. Soc.) **18**, 404 (1940).
[2] Kistiakowsky and Ransom, *J. Chem. Physics* **7**, 725 (1939).
[3] Lebedev *et al.*, *Sintet. Kauchuk* **1936**, No. 1, p. 2.
[4] Medvedev *et al.*, *Acta Physicochim.* (U.S.S.R.) **11**, 751 (1939).
[5] Young, Vogt, and Nieuwland, *Ind. Eng. Chem. Anal. Ed.* **8**, 198 (1936).

EMULSION POLYMERIZATION OF SYNTHETIC RUBBER IN 10-GRAM SYSTEMS

AN EXPERIMENTAL TECHNIQUE *

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In developing practical recipes for the manufacture of synthetic rubber, it was desirable to investigate the effects on the plymerization process of a large variety of highly purified substances. Only small quantities of many materials were available. Furthermore, to obtain valid comparisons between experiments conducted over a period of time, it was necessary to keep standardized samples of the major components and to use them as economically as possible. These considerations led to the development of a small-scale polymerization technique, whereby from 10 to 20 grams of monomers could be employed. By this method an extraordinary amount of valuable information was obtainable. This included:

1. Yield
2. A polymerization reaction curve from which to estimate length of induction period, if any; rate of polymerization at any desired time; and overall conversion at any desired time
3. Kind of emulsion, *i.e.*, whether fluid, viscous, gelatinous, or heterogeneous, at any stage in the process
4. pH of emulsion at end of process
5. Qualitative observations on coagulation
6. Production of a sample of synthetic rubber sufficiently large to determine solubility, milling characteristics, and cured properties by procedures described by Garvey[1]

This small-scale technique has been employed for investigating the polymerization of a large number of monomers and comonomer mixtures, for evaluating emulsifying agents, for determining the effect of impurities in the reagents employed, for varying the comonomer ratio and the ratio of hydrocarbons to aqueous phase, and for investigating the behavior of various initiators, inhibitors, and other ingredients of the polymerization recipe. It proved to be especially advantageous in providing information on the effect of some one ingredient over a range of concentrations. The influence of reaction temperature was readily determined. In general, the advantages of the technique were particularly apparent in:

Preliminary surveys, in which wide areas of investigation had to be covered in the shortest possible time. The method is amenable to simple labor-saving tricks, such as filling a large number of reaction tubes at the same time with solutions of a given emulsifying agent.

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Control testing of raw materials. The particular properties essential for polymerization of all shipments of materials intended for large-scale production can be tested quickly. A good correlation can be obtained between the experimental results of this method and behavior on a manufacturing scale.

The most serious limitation to this technique is that materials cannot be added to or subtracted from the system once polymerization has started. [Balandina *et al.*[2] described a similar technique, the details of which are not readily available to English-reading investigators.]

RECIPES FOR POLYMERIZING SYNTHETIC RUBBER

The development of satisfactory polymerization recipes is one of the important objectives of synthetic rubber research. Patent literature contains many examples of such. The following, from a U. S. patent issued to Wollthan and Becker[3], and recalculated to the scale of this technique, is perhaps typical:

Butadiene	7.5 grams
Styrene	2.5 grams
Isohexyl mercaptan	0.05 gram
Water	18.0 grams
Sodium oleate	2.0 grams
Ammonium persulfate	0.03 gram
Temperature	30° C
Time	"Several days"
Yield	"Excellent"

An understanding of the function of each ingredient is essential. In the above example, the butadiene and styrene are the monomers, which, by copolymerizing, form synthetic rubber. The isohexyl mercaptan is described as a substance exerting a "regulating effect", *i.e.*, it possibly decreases the branching characteristics of the resulting polymer. Sodium oleate is the emulsifying agent, and ammonium persulfate acts as a polymerization initiator, also called a "polymerization catalyst".

The possibilities of research on such a system are great, and are increased by the fact that a variation introduced in any one ingredient may require a concomitant change in some other ingredient. For example, substituting another substance for the initiator might require a change in the type of emulsifying agent employed to get satisfactory results.

GENERAL CONSIDERATIONS ON TECHNIQUE

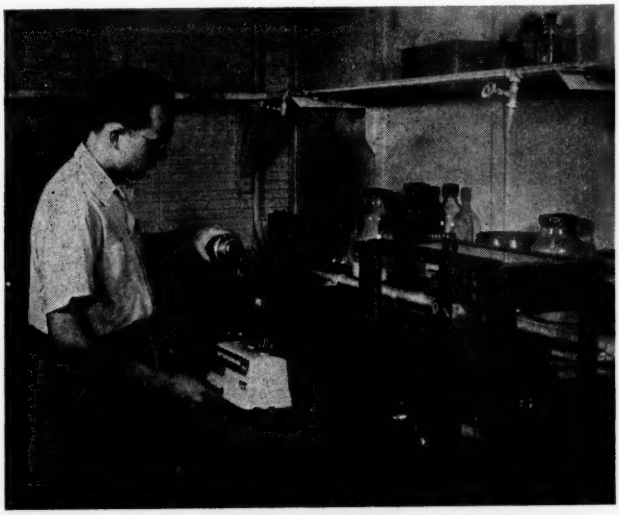
Polymerization, while a science, is also an art. The way in which things are done—that is, the niceties of experimental technique employed—is of equal importance to the scientific aspects of the subject. Unless this viewpoint is kept clearly in mind, the investigator is frequently confronted by baffling failures. Emulsion polymerization is particularly susceptible to the influence of traces of contaminants. The equipment of a research laboratory may be covered with dust which contains inhibitors or accelerators of polymerization, indeed, some substances, which under certain conditions inhibit polymerization, may under sightly different conditions act as catalysts. Nevertheless, the difficulties confronting the investigator can be avoided with a little care and forethought.

In general, solutions or other substances to be employed in polymerization experiments should not be exposed to atmospheric contamination for longer periods than necessary. Glass stoppers afford adequate protection. The

contents of a flask may be temporarily protected by covering the mouth with a sheet of clean dry tinfoil. Cork stoppers should be avoided; but if necessary, they can be covered with tinfoil. In no case should the alkaline contents of flasks come in contact with tinfoil.

Glass bottles and flasks must be clean. In most cases treatment with chromic acid cleaning solutions, followed by rinsing with tap water and then distilled water, is adequate. Reaction tubes, however, require more effective cleaning.

In one operation it is convenient to pour the volatile contents of a Dewar flask through a short length of rubber tubing. Although rubber contains



Weighing butadiene.

antioxidants, accelerators, and other chemicals, no trouble is experienced from this source if the rubber tubing is first extracted by boiling in several changes of acetone. This can be done (on a steam plate) in a covered beaker if a sizable piece of dry ice is placed on the watch crystal, which thereby becomes a convenient reflux condenser. The extracted tubing can be kept in a stoppered wide-mouthed bottle for future use.

Certain monomers can be efficiently separated from powerful inhibitors added as stabilizers by distillation through relatively simple equipment. The practice of distilling monomers in the absence of an inhibitor should be avoided because of the danger of explosions due to the accumulation of peroxides in the distillation residue.

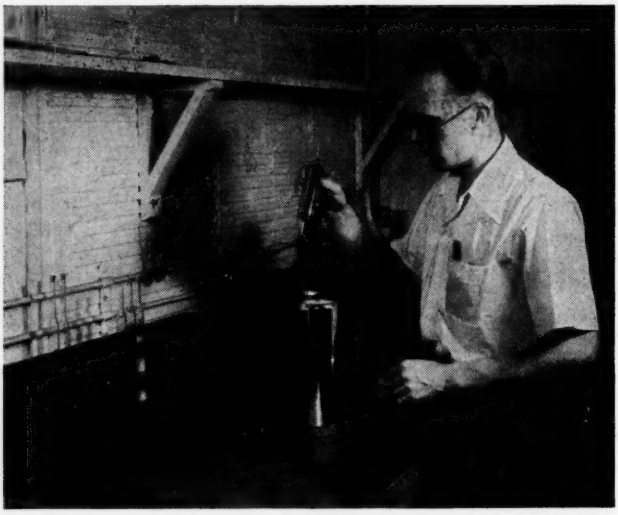
It has been customary in the laboratory to prepare fresh samples of butadiene by condensation in clean glassware from a stream of gas taken from a large cylinder of liquefied material. Higher boiling monomers are freshly prepared by atmospheric, vacuum, or steam distillation as required. All-glass distillation equipment is most satisfactory. The unstabilized monomers can be kept stoppered in a refrigerator at $-30°$ C for several days without detectable deterioration.

Sometimes repetition of an operation is advisable. Metallic polymerization vessels, no matter how carefully cleaned, may be inhibited; merely emptying and recharging are often sufficient to ensure a satisfactory reaction.

There is no substitute for constant care and cleanliness on the part of the investigator. A careful experimenter can easily adjust the weight of small portions of certain monomers, using a clean medicine dropper, while a careless experimenter (performing the same operation) can ruin a large number of experiments by allowing the monomer to come into contact with the rubber bulb of the medicine dropper.

EXPERIMENTAL PROCEDURE

The ingredients of a polymerization recipe are sealed into a test-tube, which is rotated at a constant temperature. The course of the reaction is followed by noting the decrease in volume of the system, and the latex is removed for coagulation when the polymerization has proceeded as far as desired. The yield is determined by weighing the dried, stabilized coagulum.

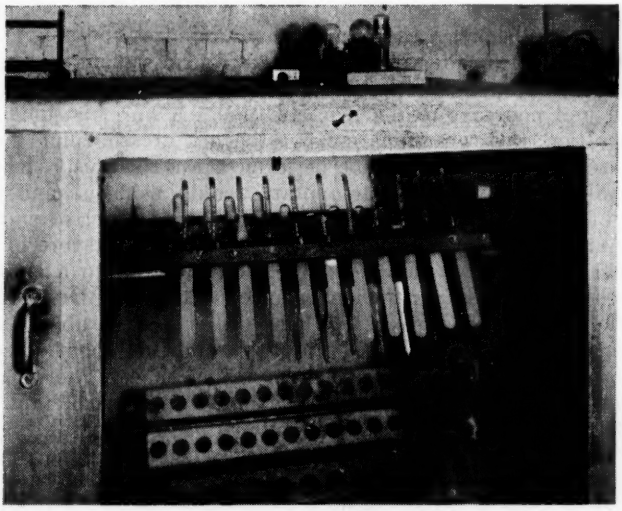


Adding butadiene to reaction tube.

Pyrex reaction tubes, 22 mm. in diameter, approximately 55 cc. in capacity, to the upper end of which are sealed 10-mm. diameter Pyrex tubes, may be obtained in gross lots from the Corning Glass Company, according to the following specifications: "Glass tubes, Pyrex, 22 mm. O.D. × 1.5 mm. walls (uniform), 215-mm. body to neck, 22-mm. tapered shoulder, 145-mm. neck. 10-mm. neck × 1-mm. wall thickness". These can be made by the experimenter, but it has been found cheaper to purchase them.

New tubes are cleaned by rinsing with distilled water and anhydrous C.P. synthetic methanol, in that order, and evacuating until dry. Evacuation may be accomplished with a Cenco Hyvac pump connected in train through a dry ice-acetone trap, which condenses the methanol and prevents diffusion of any volatile inhibitor back into the tube. Acetone-extracted rubber tubing is used to attach the reaction tubes to the vacuum system.

Old tubes, after being cleaned in a chromic acid bath, are repaired by sealing new necks of 10-mm. Pyrex tubing, 10 cm. long, to the shoulder of the tubes. The open ends are fire-polished. The tubes are then subjected to the cleaning treatment recommended by Suess, Pilch, and Rudorfer[4]. Clean concentrated nitric acid is poured into the tubes and allowed to stand from 16 to 24 hours. If the tubes are required at once, they are filled to the shoulder with nitric acid and gently heated from 15 to 30 minutes, then rinsed three times with tap water. One rinse should completely fill the tube to displace all the fumes. After two additional rinses with distilled water, the tubes may be dried with synthetic methanol and evacuated. If desired, the methanol rinse



Rotation of tubes in constant-temperature cabinet.

and evacuation can be dispensed with by allowing the distilled water to drain from the inverted tubes overnight. The dry tubes are stoppered with No. 0 corks, which have been covered with fresh tinfoil, and the tubes are kept in a clean place until used.

Solids may be added to the reaction tubes in quantities as low as 0.5 mg. from small aluminum foil weighing scoops. If duplicate quantities are to be used throughout a series of experiments, it is convenient to dissolve organic compounds in the less volatile comonomer and inorganic compounds in the aqueous solution of emulsifying agent.

The solution of emulsifying agent is generally prepared separately and added to the reaction tubes from a pipet or a graduated cylinder. Since slight variations in the ratio of monomers to aqueous phase have little effect, convenience generally dictates the use of the latter method. The volume of emulsifying agent employed may vary from 10 to 30 cc. for 10 grams of monomers.

The reaction tubes containing the emulsifying agent and other ingredients are placed in a refrigerator, inclined at an angle of 2° 8′ from horizontal, and frozen at −30° C. This inclination may be obtained by placing a piece of 10-mm. glass tubing under the necks of the tubes. Unless chilled in this position, the tubes will crack when placed in a dry ice-acetone bath. (The

cork-stoppered glass reaction tubes may be laid on a table at the proper inclination and covered with dry ice. However, any contamination of the contents by carbon dioxide will alter the pH of the soap solution and affect the reaction rate seriously.) If care is exercised, the aqueous phase can be frozen by direct immersion of the tubes in a dry ice-acetone bath, with frequent withdrawals and nearly horizontal rotations, so that the aqueous phase freezes in contact with the glass in the form of a hollow cylinder. The losses due to cracking of the glass are high and the operation is time consuming; therefore the method of freezing first described is preferred in most cases.

In the next step the frozen tubes are individually cooled further in a dry ice-acetone mixture contained in a quart-size straight-sided Dewar flask. A rubber dam is fitted over the tube and the Dewar flask, the neck of the tube extending through a hole in the dam. This minimizes contamination of the tube with escaping carbon dioxide, and holds it in a convenient vertical position.

The higher boiling comonomer is weighed to 0.1 gram into a tared, clean microbeaker and poured into the reaction tube. A buret is sometimes used for this operation, but contamination by stopcock grease should be avoided. In either case the operation must be performed in a rigorously clean manner.

Freshly distilled butadiene is temporarily contained in a pint-size Dewar fitted with a two-hole extracted rubber stopper through which extend two short glass tubes arranged for convenient pouring. The temperature of the butadiene is held at $-30°$ C. It is weighed to 0.1 gram into a small silvered Dewar weighing flask using a torsion balance. The small Dewar is then attached to the reaction tube by a short length of extracted rubber tubing, and the butadiene is poured into the reaction tube, allowing about 45 seconds for condensation of vapor before removing the rubber tube. The weighing flask has a 10-mm. neck, and is 11.5 cm. from bottom to shoulder, 35 mm. in outside diameter, 25 mm. in inside diameter, and about 16 cm. in overall length. Such flasks have been made in the laboratory, but it has been found more satisfactory to have them made by professional glass blowers.

The reaction tube is sealed, using a hand blow torch. It is advisable to do the sealing close to the open end of the neck in an oxidizing atmosphere; otherwise a carbon mirror may form on the interior surface of the tubing and prevent a tight seal. Occasionally, if condensation is not complete, a slow blue flame travels from the heated glass down into the reaction tube. It has been impossible, however, to demonstrate that this brings about any variation in the ensuing polymerization.

POLYMERIZATION

The sealed reaction tube is brought to reaction temperature by immersion in water. The height of the meniscus is determined and recorded, using a millimeter rule. The tube is then rotated at a constant temperature and readings of the meniscus height are made periodically. It is from these readings that reaction curves such as Figure 1 can be plotted.

If the polymerization is complete in less than 5 hours, a water thermostat is required to prevent temperature buildup. However, a thermostatically controlled air cabinet, provided with shafts for rotating the tubes, is more convenient.

A reaction tube, prepared as described, using the Wollthan and Becker recipe[3], will give an initial meniscus height of approximately 110 mm. During the course of polymerization, it will drop 11 mm. Since the height can be

read to 0.5 mm., this procedure provides a simple method of following the reaction rate with an accuracy of about 5 per cent. Table I shows for other recipes that the drop in height of the meniscus is directly proportional to the yield of polymer within the limits of error of the method. If the total decrease

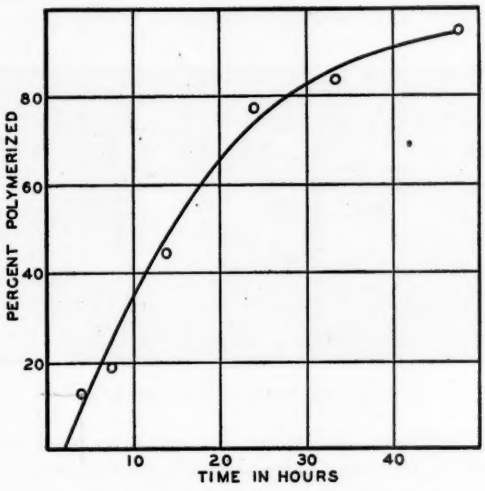


FIG. 1.—Polymerization curve.

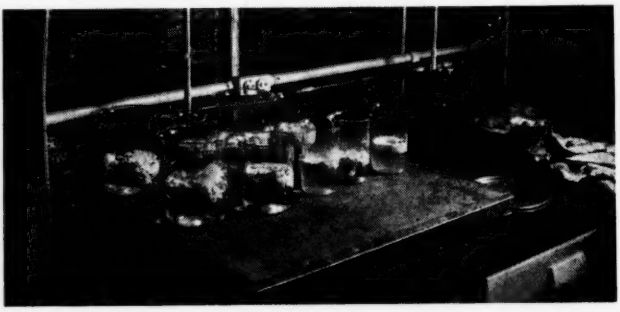
of the meniscus height is measured just before opening the tube, the yield, as measured on the dry polymer, will give an accurate basis for calculating the partial yields at any given time during the process. Reaction curves which are plotted from these figures will not be affected by errors due to variations in diameter of the individual tubes.

TABLE I

CORRELATION BETWEEN PERCENTAGE POLYMERIZED AND FALL OF MENISCUS FOR THREE POLYMERIZATION RECIPES

	Fall of meniscus (*mm.*)	Yield		Difference (%)
		Measured (%)	Calculated from meniscus (%)	
Series I	3.0	18	19	+1
	7.0	39	44	+5
	10.4	61	65	+4
	14.1	89	89	...
Series II	3.0	21	19	−2
	7.0	43	45	+2
	10.9	70	70	0
	14.4	93	93	...
Series III	2.0	9	13	+4
	4.0	20	26	+6
	4.5	26	29	+3
	5.8	38	37	−1
	7.6	44	49	+5
	7.8	47	50	+3
	11.0	67	70	+3
	12.6	86	81	−5
	14.7	94	94	...

The formation of foam, which breaks with difficulty, frequently interferes with the measurement of meniscus height. In such a case the tubes can be centrifuged by swinging in a suitable tube on the end of a 90-cm. (3-foot) rope. [According to Reynolds[5] the accuracy of this method can be improved by constriction of the tube at the position where the meniscus is read, together with high-speed centrifuging and redispersion of the emulsion by shaking after



Washing coagulated synthetic rubber samples.

the reading.] If a gel forms, or if there is much coagulation during polymerization, the height of the meniscus cannot be determined accurately.

The end of the induction period, or the beginning of polymerization, is generally indicated by the appearance of a bluish opalescence, in addition to the change in height of the meniscus.

DETERMINATION OF YIELD

Opening the reaction tubes presents no difficulty except when low partial conversions are under investigation. Then it is necessary to break the tip and direct the violently expelled foam into a large beaker. The synthetic rubber latex must next be stabilized by the addition of an antioxidant. Two per cent of dispersed phenyl-beta-naphthylamine has been found convenient and satisfactory. The dispersion of the stabilizer can be obtained by aqueous dilution of an alcoholic solution. The latex can be coagulated by any method customarily employed for breaking emulsions or coagulating natural rubber latex. Following coagulation, the rubber is washed free of soap and electrolytes, using a Büchner filter and filter paper, and dried in air, preferably at a low temperature. The yield, accurate to ± 2 per cent, can be obtained by weighing to 0.1 gram.

SUMMARY

Many manufacturers of monomers, emulsifying agents, initiators, modifiers, and other ingredients going into polymerization reactions find it necessary to have a reliable polymerization procedure for testing the quality of their products. The procedure presented, despite some shortcomings, has many advantages. Minimum amounts of material are required, and large numbers of experiments can be conducted in a relatively short time. A serious effort is made to point out some of the pitfalls which beset investigators of polymerization, regardless of the type of technique employed. The best recommendation

for the procedure described is that it has been used to develop certain types of synthetic rubber which are now in commercial production.

REFERENCES

[1] Garvey, *Ind. Eng. Chem.* **34**, 1320 (1942).
[2] Balandina *et al.*, *Bull. acad. sci. U.R.S.S., classe sci. math. nat., Ser. chim.* **1936**, 397.
[3] Wollthan and Becker, U. S. patent 2,281,613 (May 5, 1942).
[4] Suess, Pilch and Rudorfer, *Z. physik. Chem.* **179A**, 361 (1937).
[5] Reynolds, W. B., personal communication.

HARDNESS TESTING OF VULCANIZED RUBBER

III. INVESTIGATION OF THE BALL INDENTATION TEST. PART 1 *

J. R. Scott

I. INTRODUCTION

The hardness of vulcanized rubber is commonly measured by observing the depth of the indentation produced by a small ball or other indentor pressed on to the rubber by a dead weight or a spring. Up to the time of writing the readings so obtained have been merely arbitrary numbers relating to the particular instrument used. This state of affairs is unsatisfactory for two reasons: (1) the various instruments on the market use different loads and different sizes of ball or indentor, and hence give different readings for the same hardness, resulting in a confusion of arbitrary "hardness numbers"; (2) the reading gives no information as to the absolute magnitude of any known physical property of the rubber, such as would be required in designing rubber products.

The present investigation deals with hardness tests by spherical indentors under a constant load, *i.e.*, not varying with the indentation, as in some spring-loaded instruments. The object of the investigation is to determine the relationship between the depth of indentation and the diameter of the ball, the load, the elastic properties of the rubber, and the thickness of the rubber, the assumption being made, as a working hypothesis, that no other factors are involved. (Time of application of the load is not being considered at present because it can readily be standardized and its effect is small.)

The effect of thickness of the rubber has not yet been investigated, and the present experiments are mostly limited to cases where the thickness is so great that variations in it have little influence.

II. THEORY

It is convenient to consider the force required to produce an indentation on a piece of rubber as being the sum of two components: (1) the "indenting force" (D) required for the purely local deformations involved in forming a hollow in the surface of the rubber, and (2) the "compressive force" (C) required to compress the rubber between the point of indentation and the rigid supporting surface. If the total force is F, then:

$$F = D + C \tag{1}$$

On an infinitely thick piece of rubber the compressive force is zero, because any finite compression represents only an infinitesimal strain. Under these conditions F equals the indenting force, which can therefore be defined as the force required to produce a given indentation on an infinitely thick piece of rubber.

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As the present report deals with cases where the thickness is large, we have to consider only the indenting force. The magnitude of this force is evidently determined by the dimensions of the indentation and the resistance of the rubber to deformation. The latter is conveniently expressed as a ratio of stress to strain, and may be termed the hardness modulus. As the indentation is part of a sphere, its dimensions are conveniently expressed in terms of a size factor, *i.e.*, the radius of the sphere, and a shape factor, *i.e.*, the ratio of the depth of indentation (H) to the radius of the sphere (R). The magnitude of the indenting force is thus determined by three factors: (1) hardness modulus of the rubber (M), (2) size factor, *i.e.*, radius of ball (R), and (3) shape factor, H/R.

We can therefore write:

$$D = f(M, R, H/R) \tag{2}$$

(*Note:* In this and later equations, f is used to denote unknown algebraical functions of the quantities in the brackets.)

Each factor may now be considered in turn.

(1) Hardness Modulus (M)

This, being a ratio of stress to strain, must have the dimensions of force divided by (length)^2; D obviously has the dimensions of a force. Since, in Equation (2), D and M are the only terms involving force, it follows from the theory of dimensions that D must be proportional to M. Equation (2) can therefore be written:

$$D = M \cdot f(R, H/R) \tag{3}$$

The indentation can lead only to three types of deformation: extension, compression, and shear, so the hardness modulus must be a combination of the extension modulus (E), compression modulus (c), and shear modulus (S). We can, therefore, write:

$$M = xE + yc + zS \tag{3A}$$

x, y, and z are numbers depending on the relative extents to which the three types of deformation are involved; that is, they depend solely on the shape of the indentation, and are thus functions of H/R. (Friction between the ball and the rubber must have some influence on the distribution of strains and hence on x, y, and z, but tests with rubbers lubricated with castor oil show that this influence is small on large thicknesses of rubber.)

For small deformations, such as are involved in indentation, the extension and compression moduli are substantially equal[1]. (This can also be proved theoretically.)

For an isotropic, incompressible, elastic material, the shear modulus equals one-third of the extension modulus[2].

Equation (3A) therefore becomes:

$$M = xE + yE + zE/3$$

and since x, y, and z are functions of H/R:

$$M = E \cdot f(H/R)$$

Combining this with Equation (3) gives:

$$D = E \cdot f(R, H/R) \tag{4}$$

This equation shows that the force required to produce an indentation of given dimensions is proportional to the modulus of the rubber measured at small extensions. Experimental evidence in support of this is given below—Section IV, 2.

(2) Size Factor (R)

It can readily be shown that the forces required to produce equal strains in objects of geometrically similar shape but different sizes are proportional to the squares of corresponding linear dimensions of the objects. In the present case this means that for a given shape of indentation (H/R constant) the force is proportional to the square of the size factor R. Equation (4) therefore becomes:

$$D = ER^2 \cdot f(H/R) \qquad (5)$$

This equation satisfies the requirements of the theory of dimensions, since D is a force, E a force/(length)^2, R a length and H/R a number without dimensions, so that both sides of the equation have the dimensions of a force.

(3) Shape Factor (H/R)

The relationship between indenting force and shape factor, other factors remaining constant, has not yet been deduced theoretically. It has, however, been shown experimentally (see Section IV, 5; Equation (6)) that under conditions such that the compressive force (C) is relatively small, the total force F is proportional to $R^2(H/R)^{1.35}$. For a given ball size, therefore, F is proportional to $(H/R)^{1.35}$, and hence the indenting force $D(= F - C)$ must also be very nearly proportional to this quantity. Hence, the expression $f(H/R)$ in equation (5) equals $(H/R)^{1.35}$, to a fairly close approximation.

III. REVIEW OF LITERATURE

1. Relation Between Elastic Modulus and Indentation

Published data have been examined by plotting, as ordinate, the logarithm of the indentation (H) under constant load against the logarithm of the elastic modulus or rigidity (E) as abscissa. In all cases the resulting curve approximates to a downwardly sloping straight line, except that Gurney and Cameron's curve makes a sudden downward bend at the highest moduli, and Ariano's curve for rigidity at 300% is convex upwards. The slope (s) of the best straight line fitting the points is given in Table 1.

Table 1

Ball diameter	Load	E expressed as	s	Reference
$\frac{1}{16}$ inch	3 lbs.	Rigidity at 200% elongation	$-0.8\pm$	Zimmermann and Brown[3]
$\frac{1}{4}$ or $\frac{1}{2}$ inch	1000 g.	Modulus of compression	-1.6†	Gurney and Cameron[4]
10 mm.	*	Rigidity at:—		
		50% elongation	-0.39	Ariano[5]
		100% "	-0.38	
		300% "	$-0.25\pm$	

* H was measured as the "variation in indentation on passing from 1 kg. to 5.91 kg."

† Gurney and Cameron[4] state that "hardness modulus" (defined as force divided by the volume of the indentation) is proportional to $E^{2.4}$; since H is approximately proportional to the square root of the volume, it follows that H is proportional to $E^{-1.7}$, that is, $s = -1.7$ in fair agreement with the figure given above.

The wide variation between different values of s renders it impossible to draw any general conclusions.

Zimmermann and Brown's figure[3] agrees with theory because they found (see Table 2) that, for a given rubber, H is approximately proportional to

$F^{0.8}$, so in general H is proportional to $F^{0.8}E^{-0.8}$, that is, the force required to produce a given indentation is approximately proportional to the modulus, as required by theory (see Section II (1)).

TABLE 2

Rubber	Ball diameter	Loads used	n	Reference (figures refer to original papers)
Five samples, in order of increasing hardness	$\frac{5}{32}$ inch	500 and 1000 g.	0.85	Zimmermann and Brown[3]
		500, 1000, and 1500 g.	0.73 0.77 0.78 1.05 ±*	
Rubber-sulfur	5 mm. 10 mm.	Range from 200 to 1100 g.	0.78 0.79	Ariano[5] Fig. 5.
Solid tire	5 mm. 10 mm.	Range from 200 to 1100 g.	0.75 0.65	Ariano[5] Fig. 5
Tread 16 mm. thick	5 mm.	1, 2, 3, 4, 5, and 6 kg.	0.73	Ariano[5] Fig. 8
"Soft"	$\frac{1}{4}$ inch $\frac{1}{8}$ inch	Range up to 1000 g.	0.70 0.80	Gurney[6]
"Hard"	$\frac{1}{4}$ inch $\frac{1}{8}$ inch	Range up to 1000 g.	0.71 0.76	Gurney [6]
Mean of four rubbers, 9 mm. thick	$\frac{1}{4}$ inch	200, 500, 1000, and 1200 g.	0.71	Dayens, Johnson and Scott[7] Fig. 1

* Probably inaccurate because indentations were very small. The most probable value of n, excluding the figure marked * is 0.74.

TABLE 3

Instrument and load (g.) (a)	Ball diameters	Rubber (b)	r	Reference
—	$\frac{1}{8}$ and $\frac{1}{4}$ inch	—	1.414	Gurney[6] (c)
Pl; 1000	$\frac{1}{8}$ and $\frac{1}{4}$ inch	—	1.2	Pusey and Jones Corpn.[8] (d)
Pl; 1000	$\frac{1}{8}$ and $\frac{1}{4}$ inch	$H=11$	1.54	Houwink[9]
		21	1.62	
		32	1.47	
		44	1.45	
		62	1.42	
		73	1.44	
		97	1.42	
?; 2000	5 and 10 mm.	$H=60$		
		3.6 mm. thick	1.42	Ariano[5] Fig. 6
		5.3 " "	1.37	
		7.2 " "	1.40	
		9.4 " "	1.36	
		11 " "	1.36	
Pl; 1000	$\frac{1}{8}$ and $\frac{1}{4}$ inch	—	1.428	Gurney and Cameron[4] (e)
Pl; 1000	$\frac{1}{8}$ and $\frac{1}{4}$ inch	—	1.43	Gottschalk[10] (f)
Sch; 1000	5 and 10 mm.	—	1.40	
Pl; 1000	$\frac{1}{8}$ and $\frac{1}{4}$ inch	various, H from	1.39	Daynes and Scott[11] (g)
PM; 1000	$\frac{1}{8}$ and $\frac{1}{4}$ inch	6 to 100;	1.40	
RA; 1000	$\frac{1}{8}$ and $\frac{1}{4}$ inch	9 mm. thick	1.40	

Notes: (a) Pl. = Pusey and Jones plastometer; PM = Strachan piezomicrometer; RA = R.A.B.R.M. gauge; Sch. = Schopper hardness gauge.
(b) H = indentation (in mm./100) with $\frac{1}{4}$-inch ball under 1 kg.
(c) No data are given, but this figure is said to represent the ratio accurately.
(d) No data given.
(e) No data given, but a conversion table is based on this value of r.
(f) From curves representing the relationship between readings with different balls (no experimental points shown).
(g) From curves based on tests with a large number of rubbers.

2. Relation Between Force and Indentation

References 5, 7, and 8 give data on this relationship. Gurney[6] gives curves relating force with the volume of the indentation (V), and considers these to be straight lines. Actually, however, they fit much better an equation of the type, $V = \text{const.} \times F^q$, q being 1.4 and 1.45 for the "soft" and "hard" rubbers examined. The indentations corresponding to the volumes given by Gurney have been calculated and used in examining the data.

When the logarithm of the indentation is plotted as ordinate against the logarithm of the force as abscissa the points in each case lie very closely along an upwardly sloping straight line, showing that indentation (H) and force (F) are related by an equation of the type $H = \text{const.} \times F^n$.

The values of n deduced in this way are given in Table 2.

3. Relationship Between Ball Diameter and Indentation

No investigation has been made with a range of ball diameters, but data are available for the comparison of two balls with diameters in the ratio 1 : 2. The ratio (r) of the corresponding indentations is given in Table 3.

The experimental results for r, assigning due weight according to the number of samples tested, average 1.405, while the figures quoted without experimental data (excluding the obviously incorrect value 1.2) average 1.418, so the most probable value is 1.41.

IV. EXPERIMENTAL

1. Rubbers and Method Used

Many of the rubbers are referred to subsequently by serial numbers; relevant details of these are given in Table 4.

Table 4

No.	Type of rubber	Shape	Thickness (mm.)	Hardness*
1				21
2	—			44
3	—	Disc 4.5 cm. diameter	9	50
4	—			85
5	—			110
6	—			135
7	Gray buffer	Disc 8 cm. diameter	25	44
8	Gray buffer	" " "		48
9	Tire tread (gas black)	Slab 10×8 cm.	13	56
10	Tire tread (soft black)	" " "	13	104
11	Carbon black mix	Disc 4.5 cm. diameter	5	44
12	Brown sole	" " " "	5	20
13	Tread	" " " "	5	60
14	Black sole	" " " "	3.5	10
15	Flooring	Large sheet	10	33
16	Flooring	Sheet	3	25
17	Zinc oxide mix	Disc 4.5 cm. diameter	5	56
18	Magnesium carbonate mix	Disc 6 cm. diameter	12	100
19	Solid tire	Section of tire, 12×10 cm.	30	65
20	Rubber-sulfur	Disc 6 cm. diameter	10	160

Note: * Depth of indentation (mm./100) by ¼-inch ball under 1 kg.

Except where otherwise stated, tests were made with the R.A.B.R.M. hardness gauge[7]. In the tests in paragraphs 3 and 4 below, the reading was taken after the load had acted for ½ minute instead of the usual 1 minute, to save time and to reduce errors due to plastic flow. Every figure recorded is the mean of

several readings, usually five or six or more where great accuracy was required or the consistency was not so good.

As the experiments were intended as an investigation only of the indenting force, conditions were chosen, wherever possible, so as to minimize the compressive force. The indentation was, therefore, kept small compared with the thickness of the rubber.

2. Relationship Between Modulus of Rubber and Indenting Force

Experiments were made to test the theoretical deduction (Section II) that the force required to produce an indentation of given dimensions on an infinitely large mass of rubber is proportional to the modulus of the rubber measured at small extensions.

It was not possible to obtain a large number of rubbers in the form of blocks so big that they could be considered as infinite, *i.e.*, with the compressive force neglected. As, however, the compressive force must be approximately proportional to the extension modulus, other things being equal, it follows that the total force required to produce a given indentation on a finite piece of rubber must theoretically be proportional to the extension modulus. In practice, therefore, finite pieces are satisfactory for the present purpose.

Forty-two rubbers covering the whole usual range of hardness were selected. Hareness tests were made on two superposed discs 4.5 cm. diameter, total thickness about 9 mm., with a ¼-inch diameter ball and load of 1 kg., giving the reading h. From h the load (L) required to produce an indentation of 0.50 mm. was calculated by using the relationship between load and indentation for this type of test-piece (this was known from previous experiments).

The modulus (E) at small extensions was determined by finding the load required to stretch a ring (52.6 mm. inside diam., 2.25 mm. wide, 5 mm. thick) to an elongation of 5.1%. With heavily compounded rubbers this proved rather inaccurate, owing to the high permanent set and the tendency of the rubber to stretch continuously while under load.

The values of E and L are plotted against one another in Figure (*c*), (logarithmic scales are used for convenience). The broken line represents the theoretical correlation curve (L proportional to E), and it will be seen that the points lie approximately along this line. Exact proportionality between L and E in these experiments cannot be expected, for the following reasons: (1) Probable existence of grain in many of the rubbers, especially the harder ones (upper end of the graph); the modulus was measured in the plane of the sheet from which the rings were cut, but the hardness test involves the modulus perpendicular to this plane. (2) The very stiff rubbers show high permanent set and are, therefore, more or less plastic; this makes it difficult to measure the modulus accurately by the method used, and, moreover, as the theory assumes perfect elasticity the existence of plasticity must cause deviation from the predicted behavior. (3) The width of the rings was assumed to be constant, but subsequent measurements show that rings of this type vary slightly in width (2.2 to 2.3 mm.).

It may be concluded that, within the limits of accuracy imposed by the nature of the rubbers, the force required for a ball of given size to produce an indentation of given depth is proportional to the modulus of the rubber measured at small extensions, in accordance with the theoretical Equation (5).

The proportionality does not hold when the modulus is measured at higher elongations, *e.g.*, 300 per cent. This has been shown by examining data for a large number of rubbers. The same conclusion is indicated by Ariano's

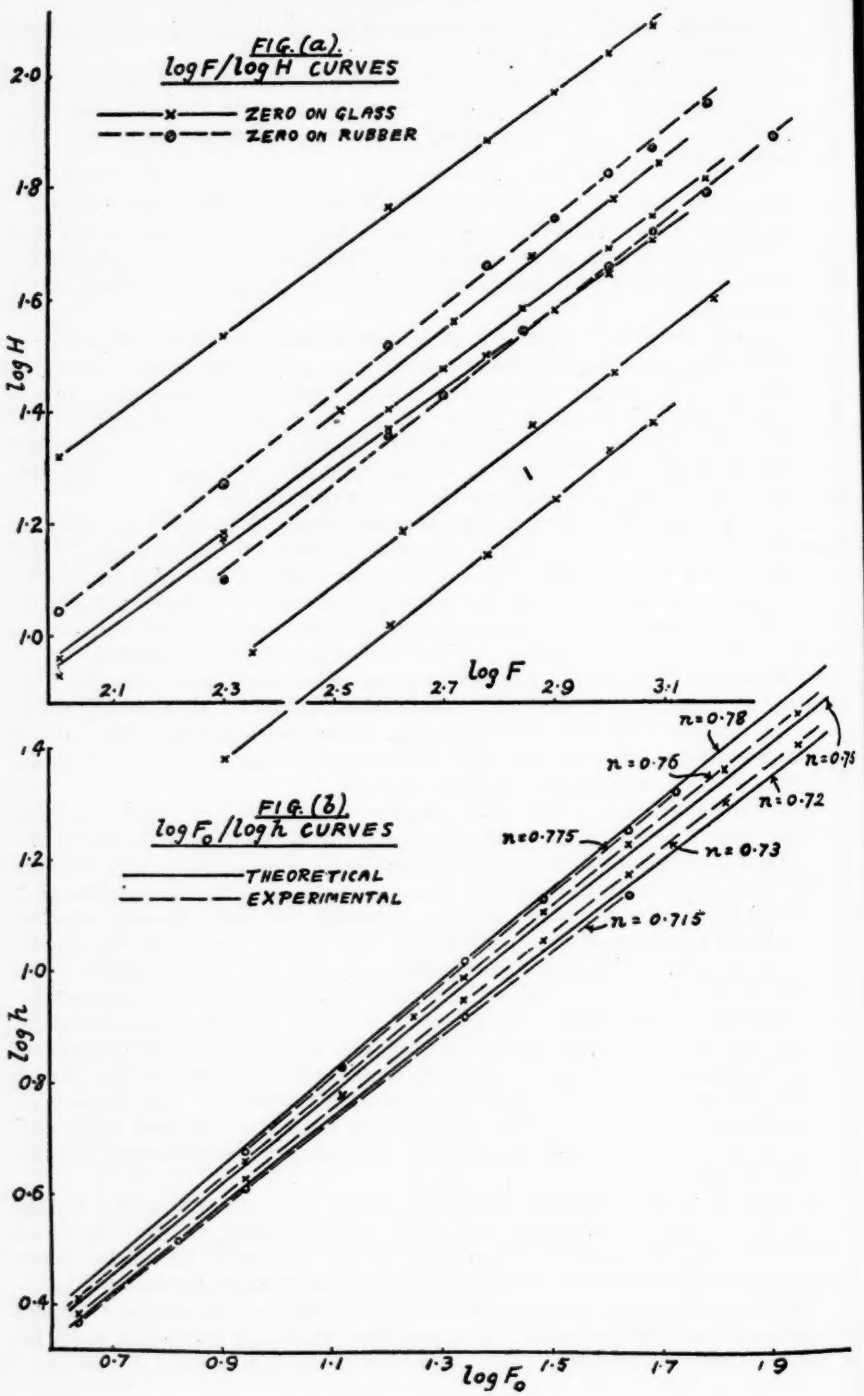


FIG. (a).
log F/log H CURVES
ZERO ON GLASS
ZERO ON RUBBER
log H
log F
2·0
1·8
1·6
1·4
1·2
1·0
2·1
2·3
2·5
2·7
2·9
3·1
FIG. (b)
log F₀/log h CURVES
THEORETICAL
EXPERIMENTAL
log h
log F₀
n=0·78
n=0·76
n=0·775
n=0·73
n=0·72
n=0·715
1·4
1·2
1·0
0·8
0·6
0·4
0·7
0·9
1·1
1·3
1·5
1·7
1·9

FIG. (c)
RELATIONSHIP BETWEEN 'E' AND 'L'

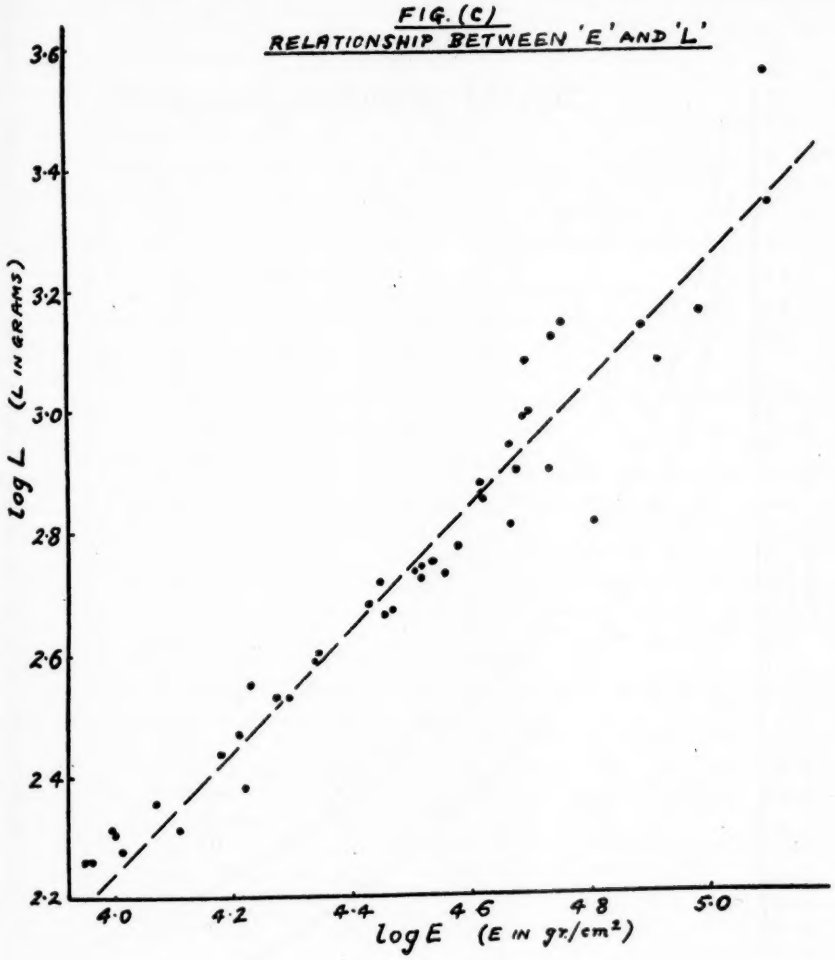
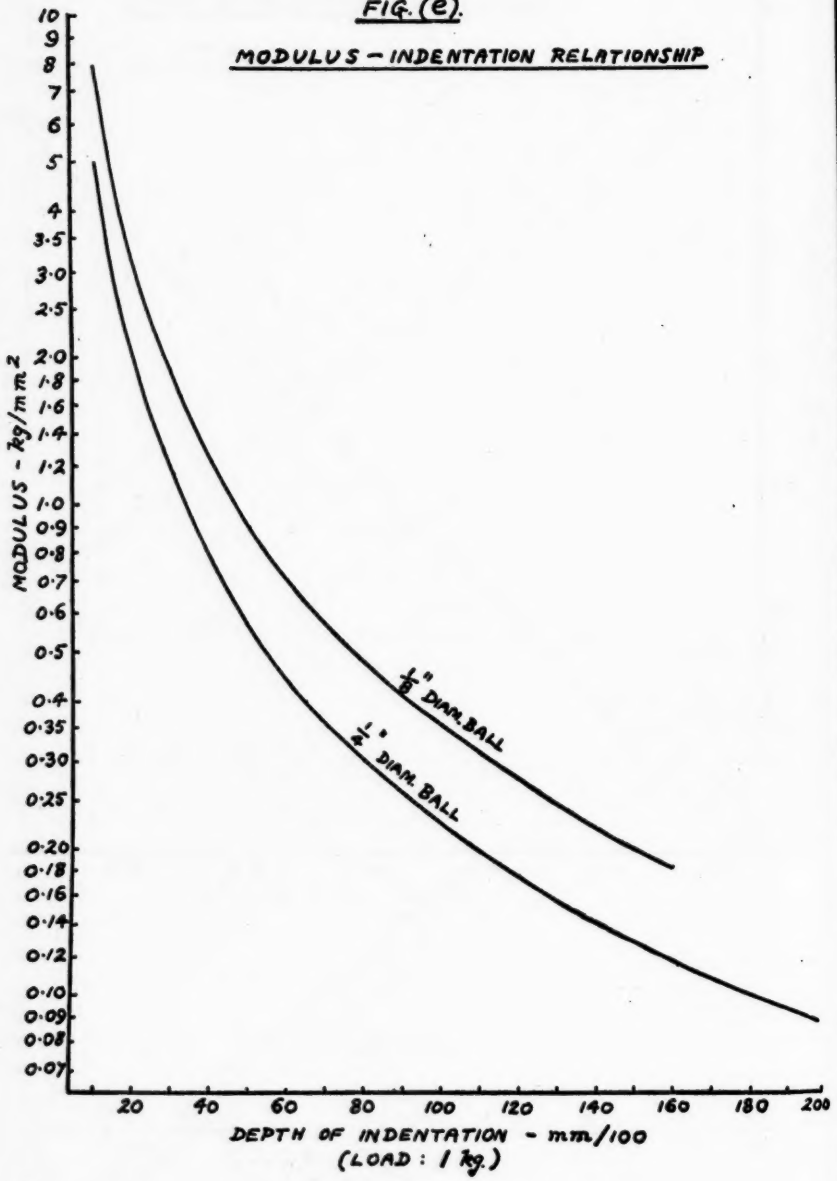


FIG. (d).

FIG. (e).

MODULUS – INDENTATION RELATIONSHIP



results in Table 1, though it is curious that Zimmermann and Brown's results, obtained at elongations comparable to those used by Ariano, do indicate approximate proportionality between modulus and force required to produce a given indentation.

3. Relationship Between Depth of Indentation and Indenting Force

(1) *Test Series A.*—Rubbers were tested with several loads, ranging usually from 100 to 1000 or 1500 g. The specimens and highest loads were chosen so that the indentation never exceeded one-fifteenth of the thickness of the rubber. The results thus represent substantially the relationship between indenting force and depth of indentation.

As the indentations under the smaller loads were necessarily very small, it was felt that errors might arise from the method used for obtaining the zero setting, *i.e.*, pressing the boss on to a glass plate, and depressing the ball until it just touches the plate[7]. If the rubber is not perfectly flat, the boss rests on the higher portions, and the ball therefore usually has to be depressed slightly below the zero position before it touches the rubber. The readings obtained thus tend to be high, and the error is proportionately greater in tests with small loads. Some tests were therefore made by another method of zero setting that eliminates this source of error. In this method the gauge stem is pressed down lightly until the ball just touches the rubber, and this position is taken as the zero. With care this can be done fairly accurately, so that the zero setting can be repeated to within 0.01 mm. It is obvious, however, that some force must be acting on the ball when it is felt to touch the rubber, so that the zero reading really corresponds to a slight indentation, and the hardness readings obtained by this method thus tend to be low.

When the logarithm of the indentation was plotted against the logarithm of the load, the points were always found to lie on a straight line, except in one or two cases where the lower end of the line showed a tendency to curve. Typical curves are shown in Figure (*a*) (H is in mm./100, F in grams). It is, therefore, evident that the relation between load (F) and indentation (H) can be expressed by a formula of the type $H = \text{const.} \times F^n$.

Table 5 gives the results obtained with the two methods of zero setting: (*a*) on glass plate, (*b*) on the rubber. The following points may be noted in

Table 5

Rubber	Ball diameter (inch)	n: Method (*a*) (zero on glass)	n: Method (*b*) (zero on rubber)
1	¼	0.77	...
2	¼	0.70	...
3	¼	0.73	...
4	¼	0.79	...
5	¼	0.76	...
6	¼	0.72	...
7	⅛	0.74	0.79
7	¼	0.72	0.76
8	⅛	0.72	0.76
9	⅛	0.78	...
9	¼	0.76	...
10	⅛	0.72	...
10	¼	0.70	...
11	⅛	0.73	...
12	⅛	0.74	...
Mean		0.74	0.77

connection with these results. (1) Method (*b*) gives higher values than method (*a*), as would be expected because the errors due to zero setting (see above) tend to make methods (*a*) and (*b*) give too low and too high values, respectively, the error being greater the smaller the load; the true value of n must therefore lie between 0.74 and 0.77. (2) Although the ⅛-inch ball always gives slightly higher values than the ¼-inch, the difference is scarcely large enough to be considered real in view of the experimental errors involved. (3) There is no evidence of any systematic change in the value of n with increasing hardness of the rubber.

(2) *Test Series B.*—As the log F/log H curves in Series A sometimes tended to deviate from linearity at small loads, additional experiments were carried out to make certain whether the relationship deduced from Series A is applicable when the indentation (and hence H/R) is small.

Tests were made on very hard rubbers using small loads, so as to get indentations not greater than 0.2 mm., the specimens being 5 mm. thick. Results obtained by methods (*a*) and (*b*) (see (1) above) are given in Table 6.

TABLE 6

Rubber	Ball diameter (inch)	Method	Indentation (mm./100) under load (g.) of 20	50	100	200	n
11	⅛	(*a*)	...	...	12.8	20.3	0.67
		(*b*)	...	...	10.4	18.0	0.79
		(*a*)*	...	...	13.7	22.1	0.70
		(*b*)*	...	...	12.3	20.4	0.74
11	¼	(*a*)	...	...	8.9	14.8	0.73
		(*b*)	...	...	7.3	13.0	0.83
12	⅛	(*a*)	...	...	10.6	17.2	0.69
		(*b*)	...	...	8.0	13.2	0.72
12	¼	(*a*)	...	...	7.1	11.6	0.71
		(*b*)	...	...	6.0	9.7	0.70
13	⅛	(*a*)	4.5	8.8	16.1	...	0.78
	¼	(*a*)	3.2	6.5	11.4	...	0.78
Mean		(*a*)					0.725
		(*b*)					0.755

* Repeat tests made some time later.

Although individual values of n vary considerably, as was to be expected with such small loads and indentations, the means for methods (*a*) and (*b*) are close to those in Series A. This shows that even at very small indentations there is no radical departure from the force-indentation relationship applicable to larger indentations.

(3) *Test Series C.*—To eliminate the difficulty of obtaining an accurate zero setting (see (1) above), experiments were made by a differential method, *i.e.*, by measuring the difference between the indentations produced by a small load f and a much larger load $(F + f)$. This difference is obviously not influenced by errors in the zero setting.

It has been shown in paragraph (1) that, under conditions where the compressive force is negligible, $H = kF^n$, at least to a first approximation. If h is the difference between the indentations produced by two loads f and $(F + f)$, it follows that $h = k(F + f)^n - kf^n$ and, therefore, $\log h = \log k + n \log F + \log [F_0 + 1)^n - 1]$ where $F_0 = F/f$. If a series of measurements

is made using a constant value of f we can write:

$$\log h = k_1 + \log [(F_0 + 1)^n - 1]$$

When h is calculated from F_0, giving n a value of the order of 0.75 and neglecting the constant term k_1, the curve obtained by plotting $\log h$ against $\log F_0$ is practically straight (actually slightly convex to the $\log h$ axis) for values of F_0 above about 5. The slope of the curve depends on the value of n.

From hardness tests with various values of F, keeping f constant, experimental $\log F_0/\log h$ curves can be constructed. These curves, like the theoretical ones, are straight or slightly convex to the $\log h$ axis. By comparing the slope of an experimental curve with the slopes (over the same range of F_0 values) of theoretical curves for various values of n it is thus possible to determine what value of n, corresponds to the experimental curve. Figure (*b*) shows theoretical curves for three values of n, together with some experimental curves. The latter have been shifted vertically to facilitate comparison.

Experiments were made in this way with several rubbers, using $f = 23$ g. and the range of F values shown (see Table 7).

TABLE 7

Rubber	Ball diameter (inch)	n	Range of loads (F) (grams)
7	1/8	0.76	100–1500
7	1/4	0.755	100–1500
8	1/8	0.73	100–1500
9	1/8	0.775	200–1200
9	1/4	0.745	200–1200
10	1/8	0.725	100–1000
10	1/4	0.715	100–1000
11	1/8	0.735	100–500
12	1/8	0.73	200–1500
Mean		0.74	

As in Series A, there is no obvious tendency for n to vary with the hardness of the rubber. The 1/8-inch ball again tends to give higher values than the 1/4-inch ball.

The mean value of n is identical with that found by method (*a*) in Series A and midway between the (*a*) and (*b*) values in Series B.

(4) *Conclusion.*—The data for the value of n are summarized as follows:

Average from literature (Table 2)	0.74
" by zero-on-glass method (Tables 5 and 6)	0.735
" by zero-on-rubber method (Tables 5 and 6)	0.76
" by differential method (Table 7)	0.74

As the zero-on-glass and zero-on-rubber figures are known to be low and high, respectively, 0.74 may be accepted as the most probable value of n. That is, on a given rubber with either 1/8 or 1/4-inch ball $H = \text{const.} \times F^{0.74}$.

4. Relationship Between Ball Diameter and Indentation

(1) *Test Series D.*—Table 8 gives the data on the ratio (r) between the 1/8 and 1/4-inch ball readings that had been obtained in the R.A.B.R.M. laboratories before the present investigation. These comprise: (1) data from Part II of the investigation[11] for experiments where the indentation did not exceed one-fifteenth of the thickness, (2) additional data that became available later from other experiments made under similar conditions. The figures from Table 6 (mean of results for methods (*a*) and (*b*)) have been included also.

TABLE 8

(Load = 1000 g. except where otherwise stated)

Indentation (mm./100)		Ratio	Instrument
½-inch ball.	¼-inch ball.	(r)	used*
4.5	3.2	1.4	RA (20 g.)
8.8	6.5	1.35	" (50 g.)
9.3	6.6	1.4	" (100 g.)
9	6	1.5	"
11.6	8.1	1.43	" (100 g.)
12>	8.5>	1.4>	Pl
13	8.5	1.53	RA
15.2	10.7	1.42	" (200 g.)
16.1	11.4	1.41	" (100 g.)
19.2	13.9	1.38	" (200 g.)
20	13	1.55	"
20	15.7	1.27	Pl
21	17	1.25	"
23.5	16	1.47	RA
23.7	16	1.48	Pl
23.5	17	1.38	PM
24.5	18	1.36	RA
26.0	18.8	1.39	Pl
26	19	1.37	"
28	18	1.55	PM
29	18.5	1.55	RA
27.8	21.4	1.30	Pl
29	20.5	1.41	"
29	21	1.38	"
30.5	21.4	1.42	"
30.7	21.2	1.45	"
40	27	1.48	RA
50	37	1.35	Pl
54	38	1.42	"

* RA = R.A.B.R.M. gauge.
Pl = Pusey and Jones plastometer.
PM = Strachan piezomicrometer.

Although individual values of r vary considerably, especially for the harder rubbers, as is to be expected on account of the relatively large errors in measuring such small indentations, there is no tendency for r to change systematically with the hardness of the rubber. This is shown by averaging the results over various ranges of hardness:

Indentation (¼ inch)	*Mean value of r*
0–10	1.42
11–20	1.425
21–29	1.405
30–54	1.425

The mean of the individual values of r in Table 8 is 1.415. As the errors of measurement are relatively larger for the smaller indentations, it might be considered more accurate to take the ratio of the sum of the ⅛-inch readings to the sum of the ¼-inch readings. This gives $r = 1.41$, so the most probable value of r is evidently between 1.41 and 1.415.

(2) *Test Series E.*—As the data for the R.A.B.R.M. gauge in Table 8 were obtained with the zero-setting on glass, which may introduce errors as explained in paragraph 3(1), further tests were made with this gauge using the differential method described in paragraph 3(3), so as to eliminate these errors.

It has been shown above that the ratio (r) between indentations produced by ⅛ and ¼-inch balls under the same load is the same, whatever the depth of the indentation. If, therefore, h is the difference between the indentations with loads $(F + f)$ and f respectively, using the ¼-inch ball, and h_1 is the corresponding difference with the ⅛-inch ball, it follows that $h_1/h = r$. The differential readings h and h_1 can, therefore, be used to determine r.

Tests by the differential method were made on several rubbers, using $f = 23$ g. and various values of F. The indentations were not allowed to exceed one-fifteenth of the thickness of the rubber. Results are given in Table 9.

TABLE 9

Rubber	Indentation (mm./100) ¼-inch ball	Indentation (mm./100) ⅛-inch ball	Ratio (r)	F (g.)
7	9.1	6.6	1.38	100
11	9.9	7.4	1.34	100
11†	10.4	7.3	1.42	100
14	14.3	10.3	1.40	1000
15	14.2	10.5	1.35	200
7	16.3	11.7	1.39	200
11	18.0	13.0	1.38	200
16	20.0	14.8	1.35	500
9	21.0	15.6	1.35	200
9*	20.1	14.9	1.35	200
17	24.0	17.1	1.40	200
17†	23.0	16.5	1.40	200
18	23	18	1.38	100
10	24.5	18	1.36	100
19	28.8	20.5	1.40	200
7	29.5	21.1	1.40	400
9	29.8	22.0	1.36	300
7	34.7	25.6	1.36	500
10	41.5	31.0	1.34	200
7	45.4	33.8	1.35	700
9	46.7	32.9	1.42	500
7‡	58	42.5	1.37	1000
7	59.5	44	1.35	1000
9	60	43.5	1.38	700
20	67.2	48.1	1.40	200
9‡	72	51.5	1.40	1000
9	80	56	1.43	1000
7	81.5	58.5	1.39	1500
10	85	63	1.35	500
9	93	66	1.41	1200
7	101.5	71.5	1.42	2000
8	107	78	1.37	2000

* Different sample of the same rubber.
† Repeat tests with another gauge.
‡ Tests with plastometer ($f = 85$ g.).

The following points must be noted in connection with these results:

(1) The value of r does not change with increasing depth of indentation. This is shown by the following averages for various ranges:

Indentation (¼-*inch*)	*Mean value of r*
0–15	1.38
16–30	1.375
31–60	1.37
70–110	1.395

This confirms the conclusion drawn from Series D.

(2) The value of r does not depend on the load, as the following averages show:

Load (F)	*Mean value of r*
100 g.	1.38
200 g.	1.375
300–500 g.	1.375
700–1000 g.	1.385
1200–2000 g.	1.40

The mean of the individual values of r is 1.380, or if the ratio of the sum of the ⅛-inch readings to the sum of the ¼-inch readings is taken (cf. 4(1) above), 1.382.

This value is rather lower than that deduced from Series D, namely, 1.41–1.415. In the latter series the plastometer and piezomicrometer figures represent differential results, since both these instruments work on the differential principle. The mean of the plastometer and piezomicrometer results is 1.39, close to the present differential results 1.38; the direct readings with the R.A.B.R.M. gauge average 1.44. This might suggest that the differential method gives a lower value of r than the direct method of observing the indentation under a given load, which would be contrary to the theoretical deduction stated above. It is considered, however, that the observed difference is due to experimental error, because in the present series of tests, which were carried out with greater accuracy, the values of r calculated directly from the indentations under the total load $(F + f)$ are not higher than 1.38, indeed if anything they tend to be slightly lower.

(3) *Conditions Giving Abnormal r Values.*—In some experiments with the R.A.B.R.M. gauge, a tendency was found for the value of r to be abnormally low, in some cases down to about 1.25, and this could not be traced to mere errors in reading or to inaccuracy in the diameter or shape of the balls.

In all these cases the indentation was very small compared with the thickness of the rubber, and the effect was noticeable particularly in tests made not far from the edge of a thick slab. The results in Table 10 illustrate how in such cases (1) the value of r becomes abnormally low at small indentations,

TABLE 10

Rubber	Thickness (mm.)	Load (F) (g.)	Differential indentation (mm./100) ⅛-inch ball	Differential indentation (mm./100) ¼-inch ball	r
7. Tested 3 to 4 cm. from edge	25	100	10.4	8.3	1.26
		200	18.4	14.3	1.29
		500	37.5	29.3	1.28
		700	48.5	37.2	1.30
		1000	63.5	48	1.33
		1500	86	64	1.34
		2000	107	78	1.37
9. Tested 1.25 cm. from edge	13	200	23.0	17.5	1.31
		500	48.1	35.5	1.35
		1000	83	59	1.41
9. Tested 4 cm. from edge	13	200	21.0	15.6	1.35
		500	46.7	32.9	1.42
		1000	30	56	1.43
15. Tested 1 cm. from edge	10	200	16.7	13.1	1.28
15. Tested 10 cm. from edge	10	200	14.2	10.5	1.35

and (2) r is lower in tests near the edge of a slab than in tests far from the edge. The results are given as the difference between the indentations under 23 grams and $(F + 23)$ g. It has not yet been determined whether the tendency to give low r values is entirely a function of the dimensions of the test-piece and the depth and position of the indentation, or whether it is a peculiarity of certain rubbers.

The following is a possible explanation of the fact that it occurs when the thickness of the rubber is very large compared with the indentation, and especially in tests near the edge. When a small ball is pressed on to the surface of a large mass of rubber, the latter probably takes the shape shown (exaggerated) in Figure (d), the indentation proper being surrounded by a relatively large depression. As the indentation is measured with reference to the surface at A, it is greater than the true indentation H by the amount d. The depression d probably depends mainly on the load and not to any great extent on the size of the ball. Hence in comparing ⅛ and ¼-inch balls, all the readings will be too high by an approximately constant amount, and the ratio will therefore be low. Proximity to the edge of the rubber doubtless increases the depression by facilitating the lateral "escape" of the underlying rubber (the results in Table 10 support this assumption), thus increasing the tendency to give low values of r. If the ball diameter, thickness of rubber, and depression (d) are all doubled, the load on the ball must be quadrupled. If now the thickness is restored to its original value, the load must be further increased to give the same value of d, and restoring the ball diameter to its original value will (presumably) have little effect. Hence, to double d, other factors remaining constant, needs the load to be more than quadrupled; that is, $d = \text{const.} \times F^p$, where p is less than 0.5. Since $H = \text{const.} \times F^{0.74}$ it follows that as F increases d becomes less important relatively to H. This explains why the tendency to abnormally low r values decreases as the load is increased.

This explanation is only tentative, as further work is required to investigate the depression effect and its dependence on the variable factors involved.

To avoid possible errors due to this effect, however, it is advisable to use a large load and small ball on not too great a thickness of rubber and not close to the edge. Errors from this cause very seldom appear in tests with the usual 1 kg. load.

(4) *Conclusion.*—The data for the value of r are summarized below:

Average from literature (Table 3)	1.41
" " previous R.A.B.R.M. work (Table 8)	1.41
" by differential method (Table 9)	1.38

Assigning due weight to these figures according to the number of tests made and their probable accuracy, the best value for r is 1.395.

5. General Relationship Between Force, Ball Diameter, Modulus of Rubber, and Indentation

The ratio between the indentations produced by balls with diameters in the ratio 1 : 2 is independent of the depth of the indentation—paragraphs 4(1) and (2). It follows that the ratio is also independent of the absolute size of the balls, provided the ratio of diameters remains the same. This conclusion is supported by the fact that the ratios for ⅛ and ¼-inch and for 5 and 10 mm. balls are practically the same (Table 3). The relationship between indentation (H) and radius of ball (R) can therefore be written in the form $H = \text{const.} \times R^m$. The value 1.395 for r (ratio of indentations with balls having diameters in the ratio 1 : 2) gives $m = 0.48$.

We therefore have:

(1) For constant force and ball size: $F = k_1 E$ (paragraph 2);
(2) " " modulus and ball size: $H = kF^{0.74}$ (paragraph 3(4));
(3) " " " and load: $H = k_2 R^{-0.48}$.

Hence, in general:

$$H = k_3 F^{0.74}/ER^{-0.48} \quad \text{or} \quad F/E = KR^{0.65}H^{1.35} \tag{6}$$

The theory of dimensions shows that F/E has the dimensions (length)^2, and hence (since K is a numerical constant) $R^{0.65}H^{1.35}$ should also have the same dimensions. Since R and H are both lengths, and 0.65 plus 1.35 equals 2.00, this condition is fulfilled exactly, thus providing a useful check on the accuracy of the experimental results.

From the experimental data given in paragraph 2, the value of K is found to be 2.1, when F is in dynes, E in dynes per sq. cm., and R and H in cm. If F is in kg., E in kg. per sq. mm., and H in mm./100, $KR^{0.65} = 0.0090$ for the ¼-inch diameter ball and 0.0057 for the ⅛-inch ball. It must be noted that these constants are calculated from the total force F required to produce an indentation 0.5 mm. deep on rubber about 9 mm. thick. As a small compressive force is thus involved, the indenting force (D) must be slightly less than F.

Figure (c) shows that the observed values of K (and $KR^{0.65}$) may deviate by ±20% from the values given above. It is not yet known to what extent these deviations are due to experimental errors, to the existence of grain and plasticity in the rubbers (see paragraph 2), or to other causes.

V. SUMMARY AND CONCLUSION

1. It is shown that the force which must be applied to a ball to produce an indentation on the surface of a large mass of rubber depends on the modulus of the rubber (at small elongations), the radius of the ball, and the ratio of the depth of the indentation to the radius of the ball. The relation of the force to the modulus and to the ball radius, the third factor remaining constant, is deduced theoretically (Section II).

2. Data from the literature on the relationships of depth of indentation to modulus, force, and ball diameter are tabulated and discussed (Section III).

3. Experiments to determine the following relationships are described: (1) modulus and force required to produce a given indentation, (2) force and depth of indentation, (3) ball diameter and depth of indentation. In connection with (2) and (3), a method of eliminating errors due to the zero setting is described (Section IV).

4. The experiments confirm the above-mentioned theoretical relationships between indenting force and modulus (approximately) and between indenting force and ball radius, and show that the force is given by the formula $KER^{0.65}H^{1.35}$ (E = modulus, R = radius of ball, H = depth of indentation). An approximate value of the constant K is deduced.

5. By using the relationship between indentation, modulus, force, and ball diameter (Section IV, 5, Equation 6), the modulus for small elongations or compressions can be calculated from the results of hardness tests. Graphs showing the relation between modulus and indentation by ⅛ and ¼-inch balls under 1 kg. load on about 1 cm. thickness of rubber are given in Figure (e). Although this method at present appears to be only approximate (errors being

up to 20%), it is sufficiently accurate for many practical purposes and hence forms a useful means of finding the modulus in cases where it is impossible to obtain test-pieces for tensile or compression tests or when an article must be tested without being damaged.

6. The results obtained make it possible to interconvert the readings of any hardness testers that use spherical indentors under constant load, whether applied in addition to a small "zero" load (as in the Pusey and Jones Plastometer) or not (as in the R.A.B.R.M. gauge). The readings (H_1 and H_2, in the same units) of two instruments using loads F_1 and F_2 applied in addition to "zero" loads f_1 and f_2, and having ball radii R_1 and R_2 are related as follows:

$$\frac{H_1}{H_2} = \frac{[(F_1 + f_1)^{0.74} - f_1^{0.74}]R_2^{0.48}}{[(F_2 + f_2)^{0.74} - f_2^{0.74}]R_1^{0.48}}$$

Where no "zero" load is used the "f" disappears.

7. Attention is drawn to certain conditions of test that give an abnormally low ratio between the readings with ⅛-inch and ¼-inch balls, and an explanation of this effect is suggested.

VI. REFERENCES

[1] Morrison, *Trans. Inst. Rubber Ind.* **7**, 112 (1931); Sheppard and Clapson, *India-Rubber J.* **82**, 312 (1931); Hencky, Natl. Mechanics Meeting of the Am. Soc. Mech. Engrs., New Haven, June 22–25, 1932; RUBBER CHEM. TECH. **6**, 217 (1933).
[2] Southwell, "Dictionary of Applied Physics", Glazebrook, London, 1922, Vol. I, p. 245.
[3] Zimmermann and Brown, *Ind. Eng. Chem.* **20**, 216 (1928).
[4] Gurney and Cameron, *India-Rubber J.* **71**, 554, 601 (1926).
[5] Ariano, *L'Industria* **43**, Nos. 17, 18, 19 (1929).
[6] Gurney, *Ind. Eng. Chem.* **13**, 707 (1921).
[7] Daynes, Johnson and Scott, *Trans. Inst. Rubber Ind.* **6**, 63 (1930).
[8] Pusey and Jones Corp., *India Rubber World* **81**, No. 3, 77, (1929).
[9] Houwink, quoted by Van Rossem, *Kautschuk* **7**, 232 (1931).
[10] Gottschalk, *Kautschuk* **8**, 144 (1932).
[11] Daynes and Scott, *J. Rubber Research* **12**, 94 (1943).

USE OF THE SHORE DUROMETER FOR MEASURING THE HARDNESS OF SYNTHETIC AND NATURAL RUBBERS *

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Two recent developments have focused attention on the Shore durometer for measuring the hardness of rubber. On the one hand, the Shore durometer readings have been made a requirement of many purchase specifications so that where they were for many years regarded as approximate values used principally for descriptive purposes, they have now become a basis for the acceptance or rejection of large deliveries of rubber goods. On the other hand, most of the synthetic rubbers now coming into large scale use show more creep than natural rubber, and this creep greatly increases the uncertainty and variation of the readings of the durometer as it is commonly used. With some synthetic rubber compounds examined at the National Bureau of Standards, the decay of the durometer reading was as much as 15 units in the first minute. The Columbian Carbon Company reported a decay of the same order of magnitude for Buna-S[1]. On account of the importance of this factor, tests have been made to show the change of Shore durometer readings with time for a series of natural and synthetic rubber compounds covering the range over which the instrument is commonly used. It is hoped that the results of these tests, together with the well-known work of Larrick[2] on the standardization of the durometer, will form the basis of a more definite specification for the use of the durometer in the determination of hardness.

APPARATUS

The apparatus shown in Figure 1 consisted essentially of a calibrated Shore durometer, Type A, meeting A.S.T.M. requirements[3], a stop watch mounted side-by-side in a frame, and a hand-operated motion picture camera. The frame was designed to hold the base plate of the durometer parallel to the base of the frame, and to permit only vertical motion of the durometer. This arrangement allowed the durometer to be applied to the specimen quickly, and permitted the load on the durometer to be varied. From one to four weights of 0.5 pound each were slipped on the vertical shaft to which the durometer was fastened. The number of these weights used for each test was the minimum required to assure firm contact between the test specimen and the base plate of the durometer.

The photographic record of the time and the durometer reading was projected on a screen by means of an enlarger. A subdivided scale was made to fit the projected image of the durometer, and with its aid the position of the pointer could be read to 0.1 unit (1/50 of the smallest graduation). The corre-

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sponding time could be read to 0.1 second from the image of the watch. The personal element was eliminated in so far as possible. The durometer was always applied to the specimen in the same manner, and the constant pressure of the base plate of the durometer on the specimen throughout any one test eliminated any error which might result from a nonuniform pressure such as may occur during hand applications lasting longer than a few seconds. Furthermore, slight tipping of the durometer was rendered impossible. Trial applica-

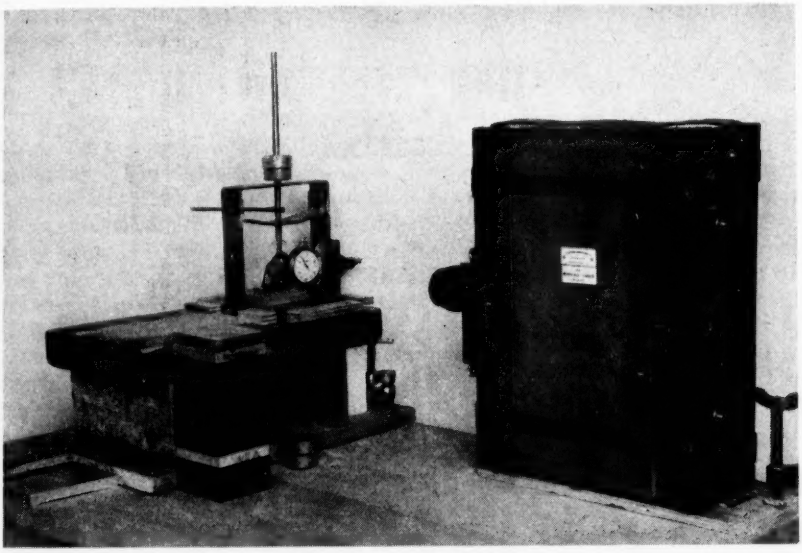

FIG. 1.—Camera setup to take simultaneous pictures of durometer and stop-watch.

tions made by hand indicated that a slight tipping of the durometer may cause a perceptible change in the reading, and may, therefore, be quite important when close tolerances are specified.

Certain limitations of accuracy arose from the nonuniform motion of the second hand of the stop-watch and from the lack of synchronism between the application of the durometer and the camera. These causes led to possible errors of the order of 0.1 second in the time of reading and sometimes resulted in failure to obtain a picture of the maximum reading of the durometer. The error in reading the time is negligible after the first 2 or 3 seconds.

Another possible source of error was the additional pressure caused by the inertia of the durometer and weights during application. As indicated by Figure 3, however, these errors were not great, and apparently had no influence beyond the first 1.5 or 2 seconds.

The exactness of the results as a whole is indicated by the conformity of the individual points to a smooth curve in practically every case and by the reproducibility of the successive tests made on the same specimen under similar conditions, as will be shown later.

TEST-SPECIMENS

The test-specimens were made from five different types of synthetic rubber and two kinds of natural rubber, and were designed to cover the range of

TABLE I

COMPOSITION OF COMPOUNDS TESTED

Formula	Ingredients (parts by weight)																	Conditions of vulcanization	
	Blended smoked sheet	Buna-S	Buna-SW[a]	Perbunan	Butyl-B 1.45[b]	Thiokol-F.1A	Castiloa	Zinc oxide[c]	Stearic acid	Agerite Powder[d]	Di-butyl Phthalate	Soft carbon black	Channel black	Tuads[e]	Altax[f]	Di-phenyl-guanidine	Captax[g]	Sulfur	Time (min.)	Steam pressure psi. (lbs. per sq. in.)
No. 1	100	...	...	...	...	...	...	5	1	...	...	...	...	...	1	...	...	3	30	40
No. 2	100	...	...	...	...	...	...	5	1	...	...	50	...	...	1	...	...	3	30	40
No. 3	100	...	...	...	...	...	...	5	1	1	...	...	50	...	1	...	...	3	30	40
No. 4	...	100	...	...	...	...	...	3	1	...	...	50	...	...	1.5	...	...	2	30	43
No. 5	...	100	...	...	...	...	...	3	1	...	...	...	50	...	1.5	...	...	2	30	43
No. 6	...	...	125	...	...	...	...	5	0.5	...	...	...	50	...	1.5	0.25	...	2.55	20	43
No. 7	...	100	...	...	...	...	...	3	1	...	...	...	90	...	1.5	...	...	2	30	43
No. 8	...	100	...	...	...	...	...	3	1	...	5	50	...	...	1.5	...	...	2	30	43
No. 9	...	...	...	100	...	...	...	5	1	...	...	...	50	...	1	...	...	2	30	40
No. 10	...	...	...	100	...	...	...	5	1	...	40	...	50	...	1	...	...	2	30	40
No. 11	...	...	...	...	100	...	...	5	3	...	...	...	...	1	...	...	0.5	1.5	45	65
No. 12	...	...	...	...	100	...	...	5	3	...	...	50	...	1	...	...	...	1.5	45	65
No. 13	...	...	...	...	100	...	...	5	3	...	...	...	50	1	...	...	0.5	1.5	40	65
No. 14	...	...	...	...	...	100	...	10	0.5	...	...	...	...	...	0.3	0.1	...	...	20	50
No. 15	...	...	...	...	...	100	...	10	0.5	...	...	50	...	...	0.3	0.1	...	...	30	50
No. 16	...	...	...	...	...	...	100	6	4	...	...	...	...	...	...	...	0.5	3.5	65	40

[a] Buna-SW contains 100 parts by weight of Buna-S and 25 of Naftolen.
[b] The zinc oxide and sulfur shown for compound No. 12 were added by the manufacturer. Compounds Nos. 11 and 13 were made from the pure polymer.
[c] Kadox variety of zinc oxide was used for all compounds except No. 12, in which the zinc oxide was added by the manufacturer, and No. 16, in which XX-Red 72 was used.
[d] Phenyl-beta-naphthylamine. [e] Tetramethylthiuram disulfide. [f] Benzothiazyl disulfide. [g] Mercaptobenzothiazole.

hardness for which the Shore durometer is commonly used. The formulas of the 16 different compounds are shown in Table I. The optimum time of vulcanization was determined for each compound in the usual way. Specimens were then vulcanized to the optimum cure in the form of square slabs 0.5 × 3 × 3 inches in dimensions.

Although considerable care was exercised to obtain homogeneous specimens, hard spots such as have frequently been observed with certain types of compounds[4] were present in some cases. The existence of these was shown by measurements not here reported. They were observed particularly in specimen No. 3.

METHODS OF TESTS

The specimen to be tested was placed on the base of the frame, and the weights on the vertical shaft were adjusted to give the desired load on the durometer. The durometer was then lowered until the indenter just touched the specimen. The stop watch and camera were then started, and the durometer was released and permitted to drop the length of the indenter or approximately 0.1 inch onto the specimen. A continuous record of about 10 frames per second was taken for the first 10 seconds, and subsequent records of 3 or 4 frames each at 15, 20, 25, 30, 40, and 50 seconds, and at 1, 1.5, 2, 3, 4, 5, 6, 7, 8, 9, and 10 minutes after the application of the durometer.

The tests were made in constant temperature rooms at ambient temperatures of 100°, 78°, and 35° F, respectively. The actual temperatures at the surfaces of the specimens were somewhat higher on account of radiation from the lamp used for illumination.

On the basis of data collected with the durometer mounted as described above, the following method was set up for all measurements taken by hand application:

1. Hold the durometer in the recommended manner[3] in the right hand, with the indenter just touching the specimen, and with the right wrist or forearm resting on the specimen or its support. Hold a watch in the left hand.
2. Make several trial applications to determine the minimum force required to seat the durometer on the specimen.
3. At the desired time apply the durometer as quickly as possible with the minimum required pressure, being careful to maintain constant pressure throughout the test and also being careful to hold the durometer motionless.
4. Take readings at 3, 5, 30, and 50 seconds after application of the durometer to the specimen.

The readings taken at 30 seconds were used as a measure of the hardness, and the readings taken at all four times were used in determining creep.

RESULTS OF TESTS

Relation of durometer readings to time:

The curves showing the durometer readings as a function of time all exhibit a rapid decrease of the readings during the first few seconds with less and less change for succeeding intervals of time. Typical curves for different types of natural and synthetic rubber of widely different hardness are given in Figure 2, and are numbered in accordance with the formulas in Table I. Although the curves are all of the same general form, the amount of decay with time

varies a great deal from one compound to another. The three curves for each sample represent three successive runs.

Curves of the form shown in Figure 2 indicate the magnitude of the creep, but do not lend themselves well to evaluating creep quantitatively. If, how-

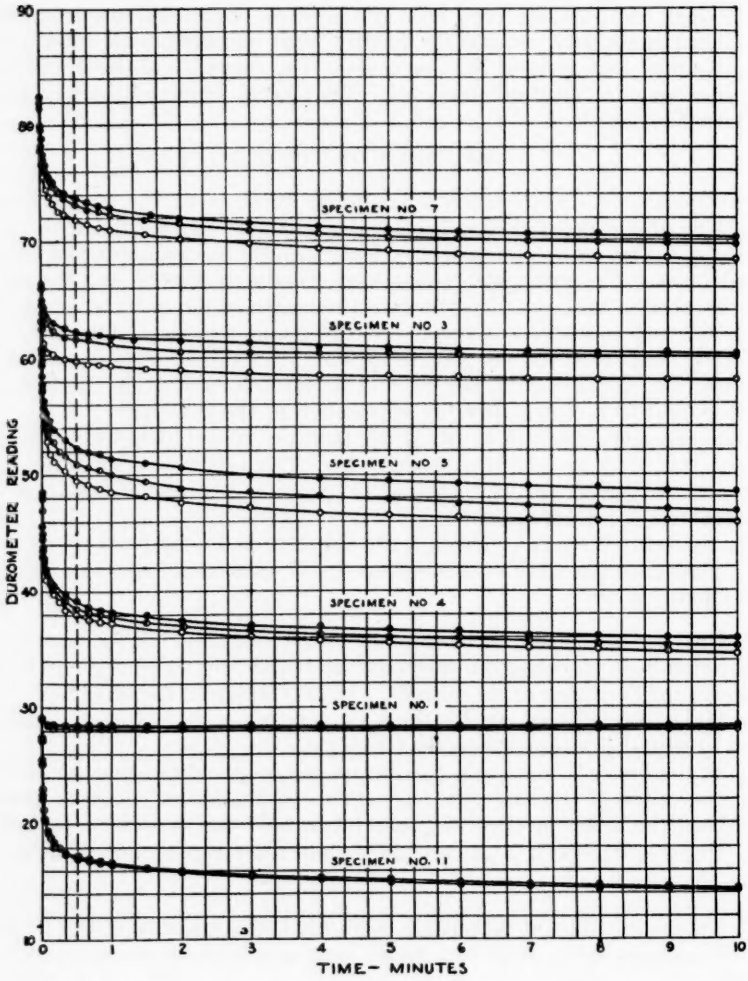

FIG. 2.—The relation of shore durometer readings to time. Three successive tests are shown for each specimen. Compounds of the specimens are given in Table I.

ever, the durometer readings are plotted against the logarithm of the time in seconds, as in Figure 3, curves are obtained which may be represented approximately by straight lines. The slopes of these straight lines afford a simple numerical measure of the creep of the different samples, as will be discussed below. The actual observations, as indicated by the points, show two small but consistent departures from a linear relation. During the first 1.5 seconds the points fall above the straight line on account of the inertia of the durometer

and its loading weights when they are dropped the length of the indenter onto the specimen. After the effect of this initial disturbance has disappeared the points deviate from a straight line by a very slight but consistent concavity upward. After the first 1.5 seconds, however, no reading was more than 0.3 unit off the straight line.

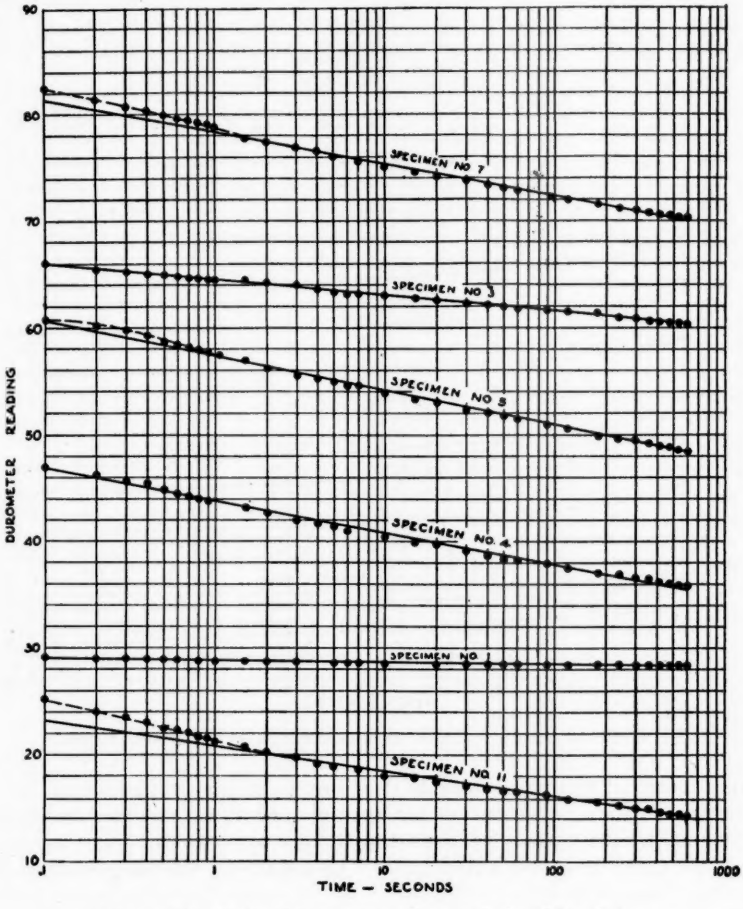

FIG. 3.—The relation of durometer readings to the logarithm of time.

Effect of temperature on durometer readings:

The foregoing tests were all made in a constant temperature room at 78° F. To determine the effect of variations in temperature, all 16 of the compounds described in Table I were also tested in rooms maintained at 100° F and 35° F. The actual temperatures of the samples were probably somewhat higher on account of the radiation from the lamp used to illuminate the durometer and the stop watch.

Typical curves are given in Figure 4 showing the change in durometer readings with time at the three temperatures. For each of the compounds shown in this figure the durometer readings are lower, the higher the tempera-

ture. The difference in the durometer readings after 30 seconds for compound No. 5 was 7 units for a change in room temperature from 35° to 100° F. For the same temperature interval, compound No. 9 showed a difference of 8 units. Other synthetic rubber compounds likewise showed relatively large temperature effects, particularly when carbon black was employed as a filler. Comparable compounds of natural rubber, on the other hand, showed differences of only 2 or 3 units between measurements made at 35° F and at 100° F. Since this difference is of about the same magnitude as variations between

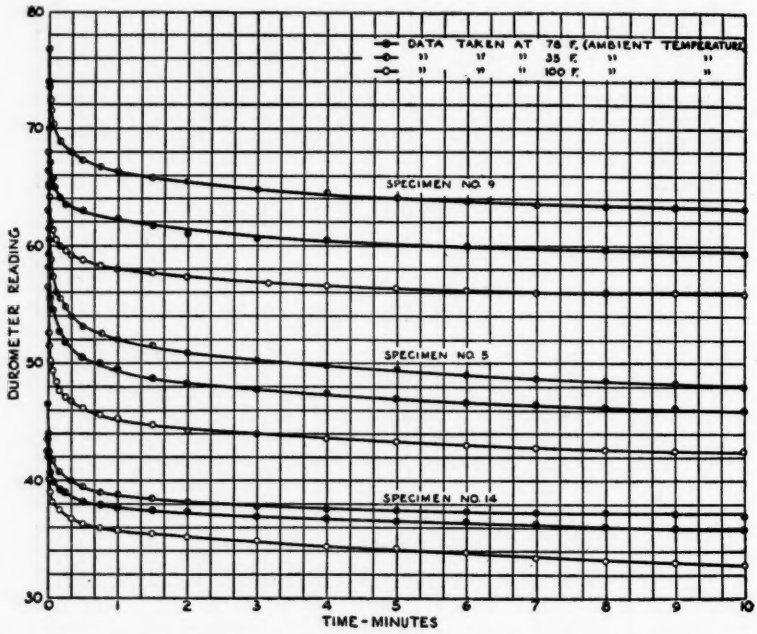

FIG. 4.—The effect of temperature on durometer readings with relation to time.

different parts of the same sample it is not particularly significant, and for this reason no illustrative curves for natural rubber are included in Figure 4. The systematic differences between the three curves for the same sample, as shown in Figure 2, is attributed mainly to change in the temperature of the specimens during the test.

DISCUSSION OF RESULTS

Use of the durometer for measuring hardness:

Figure 2 shows at a glance that if the Shore durometer is to be used for obtaining reproducible measurements of the hardness of rubber it is necessary to make the reading at a definite time after application of the instrument. The error introduced by failing to take time into account may not be large for some compounds of natural rubber, but for synthetic compounds it will, in general, be quite significant. Difficulties which have been called to our attention by manufacturers indicate that some compounds of reclaimed rubber show a creep of the same magnitude as that observed for synthetic rubbers. Although no

reclaimed rubber has been tested by means of the equipment described in this paper, simple tests by the hand application of the durometer confirm the similarity in the behavior of the reclaimed and the synthetic rubbers.

The maximum reading of the durometer is sometimes taken as a measure of the hardness. In rubbers which exhibit a considerable amount of creep, however, this reading varies with the manner of applying the instrument. If the load on the durometer is applied quickly, a higher reading is obtained than if the load is applied slowly. Consequently, it is impractical to use the maximum reading as the basis for hardness measurements. Similarly, to specify that a reading be made a few seconds (5 or less) after the application of the durometer seems undesirable because of the large error in the reading introduced by small errors in the time. If, however, a time of 30 seconds is specified, neither variations in the rate of application of the durometer nor small errors in timing have much effect. It may be seen from Figure 2 that even for a compound showing a large creep an error of 5 seconds in estimating the time interval of 30 seconds would result in an error of less than plus or minus one unit.

TABLE II

COMPARATIVE READINGS OF SHORE DUROMETER TAKEN BY SIX DIFFERENT OBSERVERS AT 30 SECONDS AFTER APPLICATION

Specimen	Observer A	Observer B	Observer C	Observer D	Observer E	Observer F	Mean	Mean deviation
No. 1	30.0	32.0	30.0	30.5	30.0	30.5	30.5	0.5
No. 2	46.0	45.5	45.5	47.0	45.0	47.0	46.0	0.7
No. 3	64.0	66.0	65.5	65.0	65.0	66.0	65.3	0.6
No. 4	41.0	41.0	39.5	39.0	40.0	41.0	40.3	0.7
No. 5	53.5	54.0	53.0	55.0	52.5	52.0	53.3	0.8
No. 6	52.0	55.0	52.0	52.5	50.0	50.0	51.9	1.3
No. 7	77.0	76.0	76.5	76.0	77.0	76.0	76.4	0.4
No. 8	42.0	42.5	41.5	41.5	40.0	40.0	41.3	0.8
No. 9	66.0	67.0	66.5	66.5	65.5	64.0	65.9	0.8
No. 10	45.5	46.0	47.0	46.5	47.5	46.0	46.4	0.6
No. 11	18.5	19.0	19.0	18.0	18.5	18.0	18.5	0.3
No. 12	41.5	42.0	40.0	43.5	42.5	40.0	41.6	1.1
No. 13	45.0	45.0	43.5	45.0	45.5	44.0	44.7	0.6
No. 14	40.0	40.5	40.5	40.0	41.0	40.0	40.3	0.3
No. 15	51.5	52.0	49.0	50.5	51.0	50.0	50.7	0.8
No. 16	30.5	32.5	32.0	31.5	30.5	32.0	31.5	0.7

The tests made at different temperatures, as shown in Figure 3, indicate the importance of controlling not only the method of using the durometer but also the temperature if the readings are to be obtained to small tolerance.

As a practical test of the method given earlier for the hand application of the durometer, six different observers were instructed to follow that method explicitly in taking durometer readings of the 16 specimens used in this investigation. Some of the observers were familiar with the durometer and others were using it for the first time. The results, which are shown in Table II, represent only one measurement on each specimen by each observer.

The maximum difference between readings made on the same specimen by any two observers was found to be 5 units. On 14 of the 16 specimens, the difference was 3 units or less. The mean deviation from the mean of the readings by the six observers ranged from 0.3 to 1.3 units. This deviation represented not only the differences in the use of the Shore instrument but also real differences between different areas in the same test-specimen. Inasmuch as the latter differences amounted to as much as 3 units for some specimens, the

agreement among the different observers was considered to be good, especially in view of the fact that each observer made only one reading on a specimen.

To determine the consistency of observation made at intervals other than 30 seconds, tests were conducted in which the durometer was applied by hand and readings were taken at the maximum indication of the pointer and at intervals of 3, 5, 30, and 50 seconds after application. As before, measurements were made by different observers on all 16 specimens. The mean deviation from the mean of all observations in each set was as follows:

	Shore units
Maximum reading	1.48
3-sec. reading	0.78
5-sec. reading	0.74
30-sec. reading	0.69
50-sec. reading	0.68

These results indicate that the maximum reading of the durometer cannot be determined with anything like as great precision as the reading at intervals of 3 seconds or longer. The precision of the reading is improved somewhat as the interval is lengthened from 3 to 50 seconds, but the improvement at the longer intervals is not conspicuous. The interval of 30 seconds is recommended for practical use so that the timing can be done by means of the second hand of an ordinary watch without exercising special care.

Use of durometer for measuring creep:

The results shown in Figure 3 indicate that, with photographic recording, the durometer can be employed to obtain a reasonably precise measurement of creep. If, however, the instrument is to be of practical use for measuring creep, it must be applied by hand and the readings taken visually.

From the observations taken at 3, 5, 30, and 50 seconds, the slope of the curve relating the durometer reading to the logarithm of the time was obtained for each specimen tested. The results of measurements by the six different

TABLE III

COMPARISON OF MEASUREMENTS OF CREEP DETERMINED BY HAND APPLICATION OF THE DUROMETER WITH THOSE DETERMINED FROM CURVES

(The slope of the curves obtained by plotting durometer readings as a function of the logarithm of time in seconds is taken as the creep)

	Creep (Shore units)							
		From observer						
Specimen	From curve	A	B	C	D	E	F	Mean
No. 1	0.2	0.5	0.0	0.5	0.0	1.0	1.0	0.5
No. 2	0.7	1.0	2.0	0.7	1.5	1.5	1.5	1.4
No. 3	1.5	1.5	2.2	1.5	2.5	2.0	2.0	1.9
No. 4	3.1	3.3	4.0	3.5	4.0	5.0	5.5	4.2
No. 5	3.3	4.2	5.5	4.0	3.7	4.2	5.0	4.4
No. 6	2.9	2.5	3.5	3.0	3.0	4.2	2.5	3.1
No. 7	3.0	3.0	3.5	3.5	3.2	4.2	4.0	3.6
No. 8	2.7	2.5	3.7	4.2	3.2	3.2	3.5	3.4
No. 9	2.5	3.0	3.2	3.0	3.5	3.7	5.0	3.6
No. 10	2.9	3.2	4.0	3.7	4.0	3.5	5.0	3.9
No. 11	2.3	2.5	3.0	2.7	3.5	3.0	2.5	2.9
No. 12	3.4	3.7	5.0	4.2	4.5	5.0	4.5	4.5
No. 13	3.7	4.0	5.2	6.5	4.5	4.7	4.5	4.9
No. 14	1.8	2.0	2.5	2.2	2.5	3.2	2.5	2.5
No. 15	2.9	2.7	4.5	4.0	4.7	4.7	3.5	4.0
No. 16	0.2	0.5	0.5	1.2	0.5	0.2	0.5	0.6

observers are compared in Table III with the values of the slopes determined from curves such as those shown in Figure 3.

The results given in the table indicate that the durometer can be employed to make a useful, though not precise, measurement of the creep in rubber. The measurements by the different observers show a relatively large scatter,

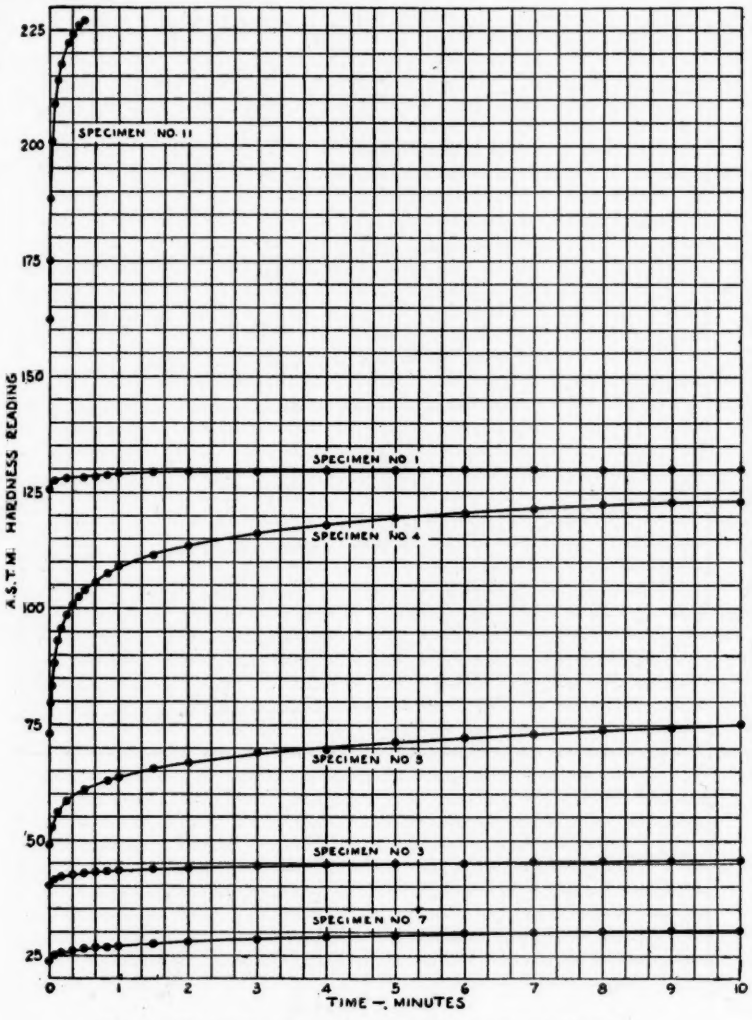

FIG. 5.—The relation of readings of A.S.T.M. hardness tester to time.

and the average values of the slopes are somewhat higher than those obtained from the curves based on photographic records. The results, however, do show clearly the increasingly greater creep in a series consisting of a pure-gum compound, a compound containing soft carbon black, and a compound containing channel black, respectively. The results also bring out the greater

creep exhibited by most synthetic rubber compounds compared with corresponding compounds of natural rubber.

APPENDIX

Advantage was taken of the photographic setup for the foregoing investigation to make similar records of the relation of hardness readings to time for the A.S.T.M. hardness tester and for a Firestone penetrometer which had been

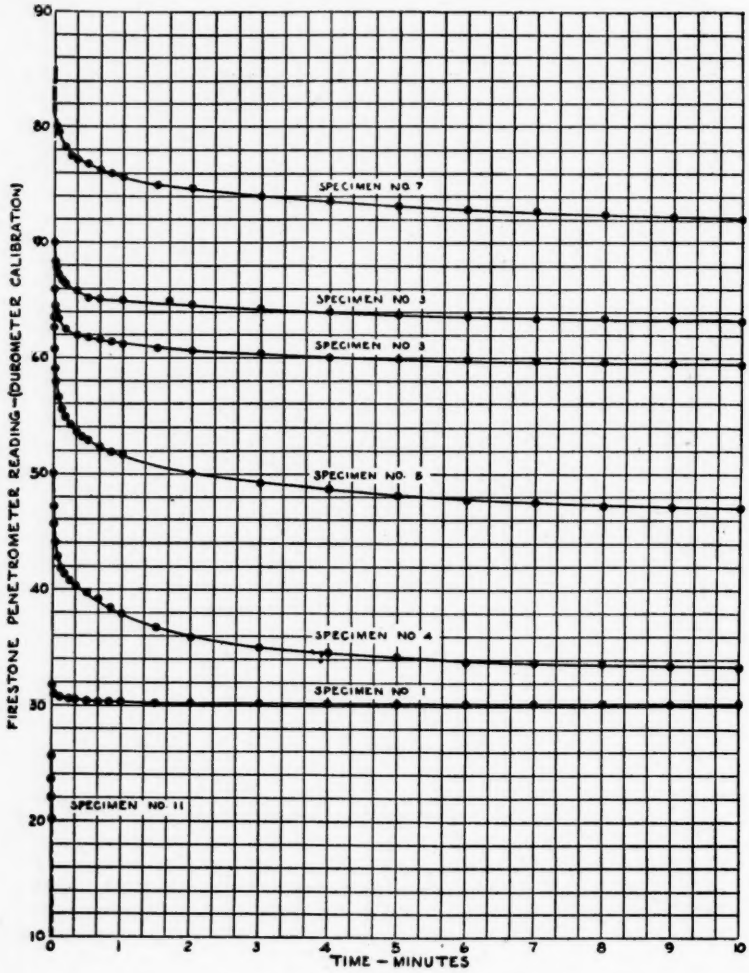

FIG. 6.—Relation of readings of a Firestone penetrometer to time.

calibrated to read in Shore durometer units. The results of typical tests with these two instruments are shown in Figures 5 and 6. The curves are numbered in accordance with the specimens, the composition of which is given in Table I. Both instruments, like the Shore durometer, show a rapid change in readings immediately after application. The rate of change decreases with time, and

when the readings are plotted against the logarithm of the time an approximately linear relation is obtained.

The chief difference between the Shore durometer and the other two instruments is that the latter show relatively greater creep for soft rubbers and less creep for harder rubbers. The reason for the difference is that both the A.S.T.M. instrument and the Firestone penetrometer employ a load which is essentially constant, whereas the Shore durometer has a high spring constant, and the load on its indenter varies from approximately 0.11 pound for maximum indentation to 1.87 pounds for zero indentation. The A.S.T.M. instrument, on the other hand, employs dead-weight loading with the same weight on the indenter for all specimens regardless of their hardness, and the Firestone instrument employs a spring having a constant so low that the actual load on the indenter varies only from 0.95 pound for maximum indentation to 1.05 pounds for zero indentation.

SUMMARY

The manner in which the readings of the Shore durometer vary with time was studied for 16 different compounds of natural and synthetic rubbers. The data were obtained from motion pictures showing a durometer and a stop watch in the same field of view. To eliminate the personal factor, the durometer was mounted in a frame, and pressure was applied by dead-weight loading. The results indicate both the necessity and the practicability of specifying that measurements be taken at a definite time after the application of the durometer to the specimen. The results also indicate the possibility of using readings taken at two different times as a rough measure of the relative creep of different rubbers.

REFERENCES

[1] "Shore creep—a new measure of logginess. The carbon reënforcement of Buna-S (GR-S)", Columbian Colloidal Carbons, Columbian Carbon Co., New York, **1943**, Vol. IV, p. 31.
[2] Larrick, "The Standardization of Durometers", *Proc. Am. Soc. Testing Materials* **40**, 1239 (1940).
[3] "A.S.T.M. Tentative Method of Test for Identification of Rubber by Means of the Durometer", D676–42T, 1942 Book of A.S.T.M. Standards, Part III, p. 1334.
[4] Howey, "Hard Spots in Vulcanized Rubber Compounds", *Ind. Eng. Chem.* **23**, 287 (1931); Kemp, Malm, Winspear and Stiratelli, "Diffusion of sulfur through rubber", *Ind. Eng. Chem.* **32**, 1075 (1940).

FROTH FLOTATION OF RUBBER AND RESIN COMPONENTS OF MILKWEED AND OTHER PLANTS THAT CONTAIN RESINS, RUBBER, BALATA, OR RELATED GUMMY SUBSTANCES *

WM. T. TURRALL, J. KLASSEN, AND H. SMEDLEY

INTRODUCTION

Separation by froth flotation of rubber-resin components from milkweed (*Asclepias syriaca*) and other plants opens a new and simplified approach to the economic extraction of resins, rubber, balata, and related gummy substances. It is well known that there is an increasing interest and potential development in the realm of resins and plastic materials. What application this method of separation will have to the simplifying of their recovery can only be surmised.

The use of froth flotation for such a separation applies the same principle in common use in mineral-dressing operations. The pulp, consisting of prepared ground plant material and water, is subjected to agitation in a common type of mechanical or pneumatic flotation cell. Air is introduced into the pulp in the form of fine bubbles that attach themselves to the rubber-resin particles, and effect a concentration of this material at the top where it is removed as froth, designated as the concentrate. The remainder of the pulp containing only a small percentage of the rubber-resin fraction is rejected and is referred to as tailings.

Various methods are being used for rubber-resin extraction from plants[1]. In one method the plant material is subjected to alkali cooking, washing, and ball-milling, to form by agglomeration worms or balls of rubber and resin that can be recovered by screening. Such methods have hitherto been limited to batch operations, whereas it is believed that froth flotation, as a means of separating the rubber-resin fraction from the cellulose and inorganic material, may make continuous operation possible.

In the investigational work, froth flotation has been conducted mainly on common milkweed. To a limited extent dogbane (*Apocynum androsaemifolium* L.), goat's-beard (*Tragopogon pratensis* L.), sow thistle (*Sonchus arvensis* L.), and a wild lettuce, provisionally identified as *Lactuca spicata* (Lam.) Hitch., also were examined.

In milkweed the rubber content varies from 1 to 4.5 per cent and the resin content from 9 to 18 per cent of the dry weight[1]. The major components of the plant are carbohydrates (cellulose, etc.), fats, and proteins. The resins and hydrocarbons are believed to be stuck to the cell walls by proteins and other colloids. Liberation may be accomplished by a water or alkali cook to break down the proteins, etc., followed by fine grinding to complete the disintegration. The alkali cook has been considered essential, but investigational work has indicated it may not be necessary if froth flotation is used to concentrate the rubber-resin.

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PREPARATION OF PULP

Different methods of preparation of pulp have been employed. The following example is one that has given satisfactory results with milkweed, and has been used as the basis for the majority of these flotation tests.

Exactly 2.5 kg. of air-dry leaves is cooked under atmospheric pressure for three to four hours with 45 liters of a 1.5 per cent caustic soda solution. This breaks down the proteins and saponifies the fats, rendering soluble approximately 60 per cent of the dry weight of the leaves. The pulp is filtered and washed with either hot or cold water until the pH is in the range of 9.5 to 10. This may take from two to six hours, but in a majority of cases four hours is sufficient. After thorough draining, the pulp consists of 1 part solids to 10 parts water. This pulp is pebble-milled for three to eight hours until the first minute worms of rubber are formed, when it is washed from the mill, using about 4 liters of water. One-half liter of this pulp has been the standard charge used in a 600-gm. laboratory subaeration froth-flotation machine. The percentage of solids in the pulp is about $1\frac{1}{4}$ per cent of the total weight.

FROTH FLOTATION

In all flotation tests it appeared advisable to float at a relatively low solid content. A solid content in the pulp exceeding 2 per cent has presented difficulties that may be overcome in future test work, but in general it was found that the rubber-resin fraction contained more cellulosic material at the higher density.

The flotation characteristics of this pulp are unique in that the pulp contains its own frothing and collecting reagents. No positive information has been established regarding the chemical identity of these reagents, but it is assumed that they may be esters, alcohols, or fat acids. Several tests have been made to improve both the grade and recovery of the rubber-resin concentrate by adding various flotation reagents having the properties of frothers, collectors, and frother-collectors. These have not produced a marked improvement, but indicate that the use of some reagents may be advisable.

The frothing conditions in the cell vary with pulp preparation. In all cases a very stable wet froth is obtained. If the pulp has had an alkali cook, a medium sized bubble results. Pulp that receives a water cook produces only very large bubbles, whereas uncooked pulp produces voluminous froth composed of very fine bubbles. Though slight frothing persists on the removal of the concentrate, tests show that the majority of the rubberr-resin fraction has been removed. Although not definitely proved, it is assumed that much of the remaining rubber-resin in the pulp is still entrapped within the cell tissue or agglomerated into worms too large to float (see Table II). If so, increased recoveries would be difficult to obtain without a modification of the preliminary treatment.

Few difficulties were encountered in the froth-flotation separation, and results indicate that this method may be of commercial importance. It should be realized, however, that much further work is necessary to establish proper conditions before ultimate grade and recovery can be obtained.

The results of a test on milkweed leaves with no flotation reagents added are shown in Table I.

In the tests recorded above, the ball-mill operation was stopped when the rubber particles had agglomerated until barely visible to the naked eye.

TABLE I

FLOTATION OF RUBBER-RESIN COMPONENTS FROM MILKWEED—NO REAGENTS, RUBBER AGGLOMERATIONS VISIBLE

Product	Weight (%)	Analyses (%)		Distribution (%)	
		Acetone extract (resins)	Benzene extract (rubber)	Acetone extract (resins)	Benzene extract (rubber)
Concentrate	24	23.0	13.5	56	75
Tailings	76	5.56	1.37	44	25
Calculated feed	100	9.67	4.22	100	100

In the test reported in Table II, similar flotation conditions prevailed, but the pulp in this case had been subjected to ball-milling operations until the rubber particles had agglomerated and some had reached the size of 2 to 3 mm. in length. The recovery of the rubber-resin components under such conditions is decidedly lower.

TABLE II

FLOTATION OF RUBBER-RESIN COMPONENTS FROM MILKWEED—NO REAGENTS, RUBBER AGGLOMERATED

Product	Weight (%)	Analyses (%)		Distribution (%)	
		Acetone extract (resins)	Benzene extract (rubber)	Acetone extract (resins)	Benzene extract (rubber)
Concentrate	20	25.1	8.2	40.5	50.6
Tailings	80	9.3	2.0	59.5	49.4
Calculated feed	100	12.5	3.3	100.0	100.0

Agglomeration takes place during ball-milling only when conditions of density and alkalinity are favorable. Under unfavorable conditions the rubber is so well dispersed through the pulp that it stubbornly resists agglomeration. The concentrate obtained by flotation yielded a good recovery of rubber on

TABLE III

FLOTATION OF RUBBER-RESIN COMPONENTS FROM AN EMULSIFIED PULP

Product	Weight (%)	Analyses (%)		Distribution (%)	
		Acetone extract (resins)	Benzene extract (rubber)	Acetone extract (resins)	Benzene extract (rubber)
Concentrate	24.3	16.90	5.67	72.3	82.2
Tailings	75.7	2.09	0.40	27.7	17.8
Calculated feed	100.0	5.69	1.68	100.0	100.0

TABLE IV

COMPARISON OF FLOTATION GRADES WITH AND WITHOUT FLOTATION REAGENTS

Reagent	Analyses (%)			
	Acetone extract (resins)		Benzene extract (rubber)	
	Concentrate	Tailings	Concentrate	Tailings
None	24.3	10.6	13.2	4.3
Oleic acid	24.0	9.7	13.3	5.3
A.C. 708	23.9	8.8	14.0	4.8
Orso	22.9	8.7	14.8	3.6
B-23	23.2	8.2	14.0	3.5
Frother 60	23.3	9.7	14.4	3.7
Pine oil	24.3	9.1	12.9	3.6

further treatment. The results of a test under such conditions are shown in Table III.

The effect of various flotation reagents in the separation of the rubber-resin constituents are summarized in Table IV.

The milkweed leaf used in this particular series of experiments was from an early July collection, at which time a suitable rubber-resin fraction had not been developed. These tests do, however, show a comparison of the grade of the products obtained with and without flotation reagents.

Table V shows the relation of the time of grind to the grade and the recovery of the rubber and resins. No alkali cook was used in the preliminary treatment.

TABLE V

EFFECT OF TIME OF GRIND ON GRADE AND RECOVERY BEFORE AGGLOMERATION

Time of milling (hrs.)	Product	Weight (%)	Analyses (%)		Distribution (%)	
			Acetone extract (resins)	Benzene extract (rubber)	Acetone extract (resins)	Benzene extract (rubber)
2	Concentrate	21	21.1	5.2	39	45
	Tailings	79	8.9	1.7	61	55
	Calculated feed	100	11.5	2.4	100	100
4	Concentrate	23	21.0	5.7	45	53
	Tailings	77	7.6	1.5	55	47
	Calculated feed	100	10.7	2.5	100	100
6	Concentrate	22	21.6	6.1	47	58
	Tailings	78	6.7	1.2	53	42
	Calculated feed	100	9.9	2.3	100	100

The results above seem to indicate that a greater percentage of the resins and rubber are being liberated and concentrated on increased grinding.

Investigational work conducted on the other named plants was done in a similar manner, and the results of flotation tests are shown in Tables VI and VII.

TABLE VI

FLOTATION TESTS ON DOGBANE, GOAT'S-BEARD, AND WILD LETTUCE WITH AN ALKALI COOK (1.5% CAUSTIC SODA)

Material	Product	Weight (%)	Analyses (%)		Distribution (%)	
			Acetone extract (resins)	Benzene extract (rubber)	Acetone extract (resins)	Benzene extract (rubber)
Dogbane*	Concentrate	11.8	35.6	14.4	38.4	63.2
	Tailings	88.2	7.6	1.12	61.6	36.8
	Calculated feed	100.0	10.9	2.69	100.0	100.0
Goat's-beard	Concentrate	17.9	27.9	3.13	82.9	83.5
	Tailings	82.1	1.26	0.13	17.1	16.5
	Calculated feed	100.0	6.03	0.67	100.0	100.0
Lactuca	Concentrate	35.2	22.8	3.51	85.3	91.0
	Tailings	64.8	2.14	0.19	14.7	9.0
	Calculated feed	100.0	9.43	1.36	100.0	100.0

* An agglomerated ball of rubber and resins was removed from the pulp before flotation.

TABLE VII

FLOTATION TESTS ON DOGBANE, GOAT'S-BEARD, SOW THISTLE, AND WILD LETTUCE WITH A WATER COOK ONLY

Material	Product	Weight (%)	Analyses (%)		Distribution (%)	
			Acetone extract (resins)	Benzene extract (rubber)	Acetone extract (resins)	Benzene extract (rubber)
Dogbane	Concentrate	30.4	37.6	12.96	80.0	91.8
	Tailings	69.6	4.12	0.50	20.0	8.2
	Calculated feed	100.0	14.31	4.29	100.0	100.0
Goat's-beard	Concentrate	4.4	20.7	1.49	40.9	49.6
	Tailings	95.6	1.38	0.07	59.1	50.4
	Calculated feed	100.0	2.23	0.13	100.0	100.0
Sow thistle	Concentrate	48.1	11.62	1.47	86.0	85.6
	Tailings	51.9	1.76	0.23	14.0	14.4
	Calculated feed	100.0	6.51	0.83	100.0	100.0
Lactuca	Concentrate	10.5	23.86	2.24	59.6	60.8
	Tailings	89.5	1.90	0.17	40.4	39.2
	Calculated feed	100.0	4.21	0.39	100.0	100.0

SUMMARY

Some of the more important features of froth flotation in the separation of rubber-resin from milkweed and other plants are summarized as follows.

1. It removes the bulk of the waste material at an early stage of the operation.

2. In the flotation of the rubber-resin component from milkweed, no additional flotation reagents are needed to cause a separation, but they have been found necessary in the flotation treatment of some other plants.

3. The grade and the recovery of the rubber-resin fractions appear to depend on the size of the agglomerates.

4. Agglomeration of the rubber-resin fraction takes place during ball-milling only when certain conditions are favorable, *e.g.*, density and alkalinity. If conditions are not favorable, the rubber-resin remains fine and well dispersed. Flotation on such a product results in the separation of a rubber-resin fraction.

5. It is not necessary to take the specific gravity of the rubber-resin components into consideration.

6. The flotation method is applicable to the concentration of the rubber-resin components from such plants as milkweed, dogbane, goat's-beard, sow thistle, wild lettuce, and possibly many other plants, with or without the use of chemicals.

7. It presents the possibility of a continuous process of rubber-resin extraction from plants.

ACKNOWLEDGMENTS

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REFERENCE

[1] Grace, Watson and Klassen, *Can. J. Research.* In press.

REPORT OF THE CRUDE RUBBER COMMITTEE, PRESENTED TO THE DIVISION OF RUBBER CHEMISTRY, APRIL 26, 1944

The Crude Rubber Committee has been asked to gather information on the properties, processing and use of wild rubbers. With the present state of affairs in the production and availability of wild rubber, the present report can cover only general observations and conclusions. As time passes and the demands of industry are felt, and as synthetic rubber production is increased and more experience is gained with it, the relative value of some types is bound to change, and a type which is used now may not be desirable some months hence.

Since wild rubbers are gathered by natives who live and work in the jungles and away from machines and transportation, it is only to be expected that there will be no uniformity of product. Foreign material is always present and any natural resins found in the latex will be found in the product. Moisture content will vary greatly from piece to piece, and variations in the degree of oxidation are to be always expected. Any data on resin content or shrinkage must therefore be considered as general observation and not a characteristic of a specific type. Curing and processing characteristics are also widely variable, and data on these also is subject to extremely wide variations.

Shrinkage is the loss in weight between the material as received and the final product after washing and drying. Some of this is due to dirt and some to moisture. Regardless of the cause, however, all wild rubbers must be washed and dried before use, so that the shrinkage is a real economic factor. Those rubbers, however, which have little foreign material compared to the moisture present, even though the degree of shrinkage is about the same, are preferable, because washing is easier and more efficient.

Resins are not removed by washing. Since a regular extraction process is needed for their removal, the final product contains a higher actual percentage of resin than the original, due to the shrinkage in weight by removal of dirt and moisture. High resin content denotes a soft rubber, and soft rubbers are very difficult to wash free of foreign material. The resin also affects the vulcanization characteristics and the processing behavior. Thus, low grade scrap rubber is always high in resin and has poor physical characteristics, such as low tensile and modulus, and also imparts a degree of softness to the uncured product. Adjustment of softener content should always be made when high-resin wild rubbers are added to a compound.

The high-grade wild rubbers can be used as a direct replacement of plantation rubbers in most cases. Thus a substitution of para or manicoba will yield a good product. Since most of the use of wild rubbers is in conjunction with synthetic, this substitution will usually have little effect, but it should always be checked. Variations in compounding and in service demands do not allow a blanket statement of the comparative behavior of any type of rubber.

The bulk of our wild rubber comes from South America, and from various botanical species. Although Africa produces a good volume of wild rubber,

there has not been so much experience gained with the African types as with the American types. Generally speaking, however, the high-grade and low-grade rubbers from either continent follow a similar pattern.

Wild rubbers should always be blended by the rubber manufacturer. In this way the effect of variations is minimized, and it is possible to utilize a small percentage of the lower grade materials. As time goes on, it is to be expected that improvements in preparation of rubber will be made, not so much by the native who gathers the original latex, but rather by processors in the market centers. Every encouragement in this direction is worth while, because encouragement of the native processor will lead him to induce the rubber tapper to improve his product. This has always been true in any product, and is not confined to rubber.

Some of the important rubbers have been examined, and the results are listed in the table below. The figures reported are averages from several actual commercial lots. Shrinkage was calculated from the difference between invoiced weight and "washed and dried" weight. The ash and resin values were determined on samples taken after washing and drying.

There are always wide differences between lots of the same type or grade because of the looseness of grading. Admixtures of botanical species other than that considered as typical of the grade are often found. There are also wide differences in methods of preparation.

The data on wild rubbers must be considered as typical and not necessarily representative of any particular shipment. Except for shrinkage, all tests, both chemical and physical, are made on material after washing and drying. With this in mind, the following table is given for its value as general information, as the range of actual values may be quite wide.

Name	Geographical origin	Botanical origin	Percentages		
			Ash	Resin	Shrinkage
Paras					
Cut fine	Brazil	Hevea	0.37	3.06	16.97
Uncut fine	"	"	0.45	3.62	19.79
Weak fine	"	"	0.38	10.38	15.30
Upriver coarse	"	"	2.12	6.24	24.24
Islands fine	"	"	0.31	4.08	13.90
Bolivian uncut	Bolivia	"	0.49	2.94	15.90
Peruvian fine	Peru	"	0.67	3.63	14.32
Scrap	Ecuador	"	0.99	4.68	17.96
	Guatamala	"	0.40	8.60	25.86
	Honduras	"	0.99	4.82	21.80
	Costa Rica	"	1.40	2.23	22.43
	Panama	"	0.70	4.05	25.75
	Columbia	"	0.82	6.20	17.38
	Nicaragua	"	1.40	6.11	19.60
Manicoba	Brazil	Manihot	4.30	3.40	20.00
Ceara	"	"	1.75	7.15	—
Mangabeira	"	Hancornia	0.58	13.07	36.45
Caucho ball	"	Castilloa			

The word "fine" denotes a clean, firm rubber. In addition to this we also have the terms "interfine", which denotes a lower grade; "sernambi rama", which is tree scrap or ground scrap; and "sernambi cameta", which is naturally coagulated latex, usually in the collection cup. The paras are also designated by district, such as "Islands", which is the district at the mouth of the Amazon, "Upriver" or "Acres", which is from the Acre region, and "Lowers", which takes in all other districts.

Most of the para is cut before being placed on the market. This is to show the condition of the interior of the biscuit. The cut fines should be completely cut on both ends. Those which are not so cut are called "san grada", and usually have a higher moisture content.

The "weak fines", which are also sometimes known as sernambi rama, contain larger amounts of resin, and so the rubber is softer than the usual fines.

The "scraps" are all rather low-grade rubbers. Ecuadorian scrap usually rates a little better than the others. All must be completely washed, and can be used in small percentages by blending with the better grades.

Manicoba often contains fine sand, but much of this material is well prepared and quite desirable.

Ceara scrap contains much bark and wood and is often difficult to clean, to an extent where the product is satisfactory.

Mangabeira is high in resin content and soft. It deteriorates very rapidly with age. This material should not be stored long in the crude state.

Castilloa yields a fairly satisfactory rubber of good properties.

All of the types listed can be obtained in a washed and dried form. When so obtained, they are ready for use without washing, but careful inspection must be made to be sure that admizture with other types has not been effected in the washing operation.

The paras will be found much more difficult to break down than the plantation rubbers. They will be more difficult to process, as they retain more "nerve" after being broken down on the mill.

There is much variation in the physical properties of the vulcanizates obtained in the A.C.S. formula. It has been found, however, that by increasing the amount of stearic acid, considerable improvement in physical properties is effected. This is shown in the table below.

The formula used is given here, and it is proposed that this formula be adopted tentatively as A.C.S. II, while the previous will be known as A.C.S. formula I. Formula II is intended for testing wild rubbers and slow curing rubbers generally. There is little doubt that physical properties can be improved by the use of activators of captax, such as amines or litharge, but these may require adjustment, and the present Formula II is a simple change.

A.C.S. Formula	I	II
Rubber (for test)	100.0	100.0
Zinc oxide	6.0	6.0
Sulfur	3.5	3.5
Stearic acid	0.5	4.0
Mercaptobenzothiazole	0.5	0.5

A comparison of the results of the two formulas in testing the rubbers above are shown at top of page 532. Comparison of the 60-minute cure at 260° F is shown.

In some cases, notably the Honduras and Panama Scrap, there is little change in properties resulting from the two formulas. The improvement in the others is evident. Why increased stearic acid improves physical properties is not exactly known, but no doubt is due to a deficiency of fat acid in the crude material.

It is interesting to compare the modulus values obtained with the two recipes at different cures. These values represent the moduli in pounds per sq. inch at 600 per cent elongation after cures of 30, 60, and 90 minutes at 260° F.

Rubber	Formula I Tensile strength (lbs. per sq. in.)	Formula I 600% Modulus (lbs. per sq. in.)	Formula II Tensile strength (lbs. per sq. in.)	Formula II 600% Modulus (lbs. per sq. in.)
Para				
Cut fine	2230	781	2940	1509
Uncut fine	2381	835	2978	1510
Weak fine	1650	700	2475	1200
Upriver coarse	1860	675	2416	1619
Islands fine	2288	1100	2885	1738
Bolivian uncut	2050	625	2250	1375
Peruvian fine	2550	950	3325	1850
Scraps				
Ecuador	1295	312	2181	632
Guatamala	775	125	2050	400
Honduras	50	50	75	75
Costa Rica	550	175	2450	375
Panama	950	225	1300	450
Columbia	502	133	1890	397
Nicaragua	240	70	1620	325
Manicoba	2892	1680	3386	1720
Ceara scrap	2850	2050	3636	2450
Mangabeira	1044	90	1950	215

Cure (min. at 260° F)	Formula I 30	Formula I 60	Formula I 90	Formula II 30	Formula II 60	Formula II 90
Rubber						
Para						
Cut fine	628	781	864	893	1509	1784
Uncut fine	700	835	940	945	1510	2088
Weak fine	475	700	750	575	1200	1200
Upriver coarse	600	675	744	888	1619	2050
Islands fine	850	1100	1200	960	1738	2510
Bolivian	400	625	675	825	1375	1800
Peruvian	625	950	1000	1025	1850	2200
Scraps						
Ecuador	145	312	386	275	632	888
Guatamala	—	125	275	150	400	675
Honduras	No cure	50	100	No cure	75	125
Costa Rica	100	175	75	200	375	425
Panama	75	225	275	150	450	675
Columbia	No cure	133	228	130	397	730
Nicaragua	37	70	90	135	325	405
Manicoba	1200	1680	1685	1165	1720	1895
Ceara scrap	1662	2050	2050	1780	2450	2712
Mangabeira	45	90	103	105	215	235

The results of Formula II do not show overcures at the longer cure.

The African rubbers have not been studied in detail. However, George Martin of the Imperial Institute has given a very careful study of this subject, and it has been published in the *Transactions of the Institution of the Rubber Industry*, Vol. 19, No. 1, pages 38–52, June 1943, and in RUBBER CHEMISTRY AND TECHNOLOGY, Vol. 17, No. 1, pages 240–252, January 1944.

In conclusion, the Crude Rubber Committee wants to point out that the data in this report are representative of the samples tested. Other lots may vary widely from those shown, and a larger volume of information would be helpful in widening our knowledge of wild rubbers. Any data, therefore, which members may have should be sent to the Chairman of the Committee, and an attempt will be made to analyze them and publish the results for the benefit of all members of the Division of Rubber Chemistry of the American Chemical Society.

G. A. SACKETT,
Chairman

ARTIFICIAL LATICES *

E. W. MADGE

An artificial latex is usually understood to mean one prepared by the inversion of the solid plastic, and the main purpose of this paper is to consider latices of this type, although towards the end some attention is given to the synthetic latices.

Given the right conditions of dispersion and the correct dispersing agents, satisfactory aqueous dispersions may be prepared from almost any plastic substance. In dispersion processes generally the material to be dispersed may occur as a liquid, as a solid, or as a plastic which is physically intermediate between the two. In all such processes machinery is required capable of inducing a shear at the point of dispersion.

It is a relatively simple matter to prepare an aqueous dispersion of a liquid. The technician has at his disposal several types of high-speed colloid mills in which the liquid is subjected to high shearing forces in the presence of suitable colloids. For solids in hard homogeneous massive form, not merely present as aggregates of otherwise fine particles, grinding machinery is necessary. For the intermediate plastics, relatively heavy machinery capable of inducing shearing forces in the material itself is required. Consequently, if the plastic substance can be rendered fluid by solution in a suitable solvent, it can be dispersed by passage through some form of standard colloid mill. On the other hand, if it can be rendered friable by loading with large proportions of powder, it may be dispersed with the aid of some form of grinding machinery. Both methods were practised by the earlier investigators, and in both cases dispersions were obtained in which an undesirable ingredient was present in large quantities. The solvent could, of course, be distilled off, but its use and recovery was an unnecessary expense and the final dispersion was not always controllable as regards stability.

Much credit is due to Americans for the discovery of the direct inversion process for plastics. This development is associated with the name of William Beach Pratt, who in 1923 took out patents describing the results of his investigations. Pratt claimed a process for dispersing coagulated rubber or the like in water, in which water was introduced into the rubber mass, and the rubber mass stretched in the presence of water, or water and a water colloid, or water and a lubricating agent or soapy substance, until the mass separated into its constituent globules. Pratt favored liberal amounts of such materials as bentonite clay, saponin, soap, glue, etc., and although these still find favor today, the amount and kind of dispersing agent is chosen with more regard to the finished product than in the early days. Pratt believed that, in the case of crude rubber, the original latex particles never lost their identity and that all that happened was a rehabilitation of the particles by softening and dissolving the protein linkages. This view, which is even today quoted freely in the literature, has little, if any, evidence to support it and is completely untenable if only on the grounds that the inversion process can be carried through with

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equal ease, using plastics in which the previous existence of discrete particles can be definitely rejected.

The following constitutes a more detailed examination of the inversion process as applied particularly to smoked sheet.

The first essential consideration is that of the plasticity of the raw material. This is extremely important. Only two sets of forces are available with which to offset the cohesive forces in the plastic and so to bring about the inversion. These are the intramolecular forces brought into play by the dispersing agents employed and the mechanical forces due to the action of the dispersing machine itself. Consequently there is an upper limit to the plasticity for a given set of dispersing conditions above which inversion cannot be brought about.

It was remarked in the literature some time ago that the more plastic the material, the finer the particles produced and the more stable the resulting dispersion. On the other hand the rubber batch can also be too soft for uniform working. With very soft batches, although water subsequently added is readily taken up, considerable amounts are as readily expressed. For smoked sheet, therefore, a uniform final product demands an accurately controlled plasticity of the raw material, which for ordinary rubber practice is rather on the low side. Obviously it is desirable to masticate only just sufficiently to make a smooth running and workable process, for otherwise the final rubber obtained from the finished dispersion will be unnecessarily weak and even sticky.

There are several other methods that can be adopted to increase the plasticity and reduce the cohesive forces in the rubber. Klein in 1921 took out a patent[1] for a dispersion process in which a soap was formed *in situ*. Pratt had already used an *in situ* process for dispersing rubber solution, but the application to the direct process for rubber inversion has certain advantages.

The *in situ* method enables advantage to be taken of the plasticity imparted by the fat acid to the rubber batch, particularly when it is readily soluble in the rubber. Moreover, this fat acid can be added easily on a mill, a procedure which is difficult with the fully formed soap. Again, the presence of the fat acid rather than that of the fully formed soap facilitates the subsequent take-up of the water into the batch.

The addition of the water itself in the later stages of the process and changes due to alteration in temperature serve as further means of modifying the plasticity.

Thus in using the *in situ* process, when masticating and mill mixing are completed, a batch is obtained containing fat acid together with, if desired, other nonaqueous dispersing agents such as bentonite clay, all of which may be readily added on the mill. Other aqueous ingredients and the water itself have now to be added. For the rubber manufacturer, the immediate temptation is to use a roll mill for these additions. A mill has many disadvantages, all of which make the use of a mill impracticable for a material with the nerve of masticated smoked sheet. For example, it is necessary to add the aqueous ingredients with the batch hot, partly because under these conditions absorption is more rapid, and any tendency for the batch to break may be rapidly overcome, and partly because when the metal of the machine is hot the metal surface is dry, and slippage is reduced to a minimum. Even under these conditions water additions on a mill are slow, and with the large evaporating surface presented, much water is lost. Moreover, as increased quantities of water are included in the batch, it is difficult to keep the batch on the rolls if rolls of a reasonably large size are employed. If by strenuous efforts the batch

can be brought to the inversion stage on a mill, the lack of uniformity of temperature throughout the batch gives rise to a nonhomogeneous dispersion, and a mill is the last type of machine on which to handle a fluid paste.

For these reasons, therefore, it is necessary, for making the aqueous additions, to transfer the mill-mixed batch containing the nonaqueous ingredients to some form of internal mixer. Such a mixer should have steam and cold water on both blades and jacket. As it has been shown to be desirable to have the mixing machine hot during the aqueous additions, the steam is turned on before adding the batch, which preferably is added warm from the mill. It is easy to make an excellent dispersion using a soap alone, but if other colloids such as casein or glue are required for special purposes, these are added before the water, preferably as concentrated solutions. The water is now added. This may be run in directly from a reservoir as fast as the batch will take it. As the batch distends with water, it becomes much softer and its mechanical strength is considerably reduced. The more water is put in, the faster the batch takes it up. The best time to form the soap, therefore, is obviously when the batch has the least tendency to break, *i.e.*, when all the water is in. Sufficient water is added to bring the concentration to approximately 75 per cent.

The soap is now formed preferably by the addition of a small quantity of caustic alkali. Potash is usually preferred. The potash is added as a strong solution to reduce the volume and time of addition.

The batch, still hot and containing all the fully formed dispersing agents, is now voluminous and is distended and soft.

The second important condition governing the production of a good aqueous dispersion by the inversion process must now be met. This is that a good dispersion of rubber in water cannot be realized unless first of all a good dispersion of water in the rubber is obtained. This condition is realized simply. Cold water is turned on both blades and jacket, and the batch is cold-worked until a fine dispersion of water in the rubber is obtained. As the temperature falls and the working proceeds, the batch naturally gets stronger, and all sponginess and crumbiness disappears. Everything is now ready for the actual inversion. Steam is turned on jacket and blades, and as the temperature rises, inversion takes place relatively sharply. This change is quite spectacular. One minute the mass is elastic and rubbery, and the next minute is a stiff aqueous paste which may be smoothed out on the hand like a stiff cream. When inversion is complete (the concentration is still about 75 per cent), ammonia water is gradually added for dilution, slowly at first and then faster, cooling at the same time. Should the mixer be cooled without dilution being effected, the mass would simply revert to its elastic condition. The dispersion is now adjusted to concentration and, after sieving, is ready for use.

It is, of course, relatively easy to produce a fair dispersion from a plastic material such as a reclaim, but the consecutive and consistent production of large scale batches of dispersions uniform at a particle size of say 3 to 4 μ from a nervy material such as smoked sheet requires considerable scientific control, particularly when it is essential to keep the content of the dispersing agent to a minimum to condition the properties of the final dispersion.

Machinery.—Before examining other aspects of the dispersion process and dispersions of other plastics and their properties, consideration should be given to the question of suitable machinery. The limitations of roll mills have already been indicated. Obviously a technician who wishes to tackle disper-

sions of various types must have at his command an internal mixer capable of rapid and uniform heating and cooling. It is important, however, to notice that the best blades for the earlier stages of the process are not necessarily ideal for the dilution stage, which really demands a paddle type blade as in a dough hopper. This difficulty has to a large extent been overcome by removing the batch as soon as it has been just sufficiently diluted to prevent reversion, in which form it is quite a stiff paste. This is transferred to suitable containers fitted with high-speed stirrers in which dilution is rapidly and efficiently effected. Such a procedure is effective in smoothing the dispersion. Alternatively, a diluting hopper could be used fitted with paddle blades.

Some idea of the mechanical behavior of a suitable internal mixer can be gained from power consumption figures obtained by one of the writer's colleagues during rubber inversion runs. The maximum power consumed was, as might be expected, during loading and warming. The masticated and mixed batch running in the mixer before any aqueous additions gave a load of about 0.3 horse power per pound of compound. As the aqueous ingredients were added the load steadily dropped. Any tendency to break the batch due to indiscrete additions were clearly shown up by a sudden falling off in load. With the aqueous addition made and the load now only about a sixth of the original, a slight rise was experienced during the cold working period. Then when the inversion period was reached the load fell away to a minimum, the governing condition then being one of rapid and uniform heat transfer rather than a mechanical one.

It will, therefore, be seen that a heavy mixer is only really required when the batch is behaving more or less like a rubber batch. Concentrated thinking and experiment could well be directed toward the design of machines best suited to dispersing rubber and other plastics; at present it is necessary to make the best of any available compromise. The ideal machine should carry the same load more or less throughout the whole dispersion process.

The dispersion of reclaim and rubber substitutes.—Reclaim is more plastic than rubber and, consequently, the control conditions are less stringent in comparison with those necessary for the dispersion of smoked sheet. In addition the changes wrought by temperature are less pronounced, and in some ways the whole process is easier.

Hence efforts should be directed chiefly to the second condition laid down for the production of a good aqueous dispersion, namely, that of obtaining a good and uniform dispersion of the water in the reclaim before inversion. In the case of reclaim, however, there are one or two other considerations which arise from the nature of the reclaim itself. The reclaim must be as uniform as possible, that is, its grinding and refining must have been adequate during its manufacture. No dispersing process will remove unreclaimed or less reclaimed vulcanized bits that are present, and these will have to be sieved out of the final dispersion. Reclaims also may contain appreciable quantities of whiting, zinc oxide and the like which will have an effect on anionic dispersing agents that may be employed. The use of sodium carbonate or sodium silicate is thus advantageous.

It will be appreciated that the easiest reclaims to disperse are the alkali reclaims, although thermal reclaims also behave well.

The dispersion of factice is also a relatively easy process. Factice is friable in nature, and to provide a smoothly working batch in the internal mixer for the dispersion of the water in the plastic, a small amount of binding agent is required, such as for example, a small amount of rubber. The particle size of

factice dispersions is in general smaller than that of rubber or reclaim dispersions, and the viscosity is also in general lower.

General properties of artificial dispersions.—As the dispersions have been artificially prepared, the properties of a particular dispersion depend to a large extent on the raw material and the ingredients used for dispersing it.

Even so, over the wide range of substances normally employed for various types of artificial dispersions, certain general characteristics may be examined in comparison with those of commercial rubber latex.

Due to the method of preparation, there is no difficulty in preparing dispersions at concentrations appreciably above 60 per cent. The viscosity of such dispersions depends on their concentration but at similar concentrations, that is, at similar total solids contents, the viscosity of an artificial dispersion of rubber is appreciably greater than that of natural rubber latex. The divergence increases, as might be expected, as the concentration rises. Nelson[2] quotes the following figures:

	Rubber latex			Artificial dispersion	
	Normal	Centrifuged	Creamed	Pale crêpe and smoked sheet	Reclaim tube and whole tire
Total solids (%)	37.5–40.5	61–64	60–65	55	50–60
Viscosity (centipoises)	4–4.5	30–50	30–60	100	100

If the viscosities are compared at similar dry rubber contents, that of the artificial dispersion is still greater than that of natural concentrate, although the effect is not so marked.

The cause of the increase in viscosity is the presence of hydrophilic colloids, chiefly soaps, used in the preparation of the artificial dispersions. If similar quantities of the same colloids are added to natural latex, a large increase in viscosity may be observed.

Air retention is enhanced by the presence of capillary active dispersing agents, and until it is removed, the air adds its own contribution to the viscosity figure.

Obviously the way to meet this difficulty is to reduce the content of dispersing agents to the lowest permissible figure. It is regretted that, with one or two notable exceptions, most of the recipes given in the literature quote incredibly large quantities of dispersing agent. This may ensure an easier passage in the actual dispersion process, but the resulting product has a greatly reduced commercial value.

One of the chief differences between an artificial rubber dispersion and natural latex is the lack of a really strong bond, that is, an adsorption bond between the rubber particle and the dispersing and/or protective colloid. There is much evidence and there are many speculations, not all based on the evidence, concerning the structure of the natural latex particle. Broadly it may be said that the natural latex particle depends for its stability and charge on the compound protection of protein, fat acid soaps and other substances.

Baker[3] concluded that about 0.02 per cent nitrogen (calculated on the rubber) was associated with the rubber globules themselves, whereas at the particle boundary were concentrated protein soaps and other surface active substances, probably of lipoid nature. It is likely that the lipoid portion is next to the rubber phase, with the hydrophilic proteins and soaps on the outside.

The general inference, therefore, is that the protective agents in the case of natural rubber latex are held strongly to the particle and in contradistinction

in the case of the artificial dispersion the bond is much weaker. This view is demonstrated by dilution tests. If a container containing a standard type of dispersion is swilled out with large volumes of water, residual adherent floccules are frequently formed. Dispersions of a particle size of 5 μ upwards are particularly prone to dilution instability. Finer dispersions, however, undergo severe dilution down to $\frac{1}{2}$ per cent concentration or below without difficulty. The steps to be taken to obtain really fine dispersions have already been discussed. If flocculable dispersions are diluted with a dilute soap solution, no flocculation results, indicating that these dispersions are largely stable because of an equilibrium with the dispersion medium. If this equilibrium is seriously disturbed then the dispersion becomes unstable. In other words, with the usual fat acid soap, the maximum ionic concentration at the interface is not high, and soap is removed as dilution increases.

Various methods of raising the ionic concentration at the interface are known. One of these in particular has been applied to the dispersion of rubber. This depends on the known method of introducing a linking into a straight paraffin chain salt by the use of a substance such as chloresterol. In the patent of Blow[4] the straight paraffin chain salt is sodium cetyl sulfate, and the chloresterol is in the form of wool wax.

It has also been found that bentonite clay when milled initially into the rubber is helpful in maintaining the stability of the finished dispersion on dilution. Here again the bentonite is probably quite strongly anchored to the rubber particle.

Artificial dispersions of rubber may be creamed or centrifuged, using standard methods in a similar manner to normal latex. The creaming or centrifuging does not differ in kind but in degree. Such methods have been proposed as a means of purifying artificial dispersions from a part of what may be a relatively higher proportion of colloid originally present in the dispersion. In general, the maximum concentrations obtained during multicreaming or multicentrifuging processes are appreciably below those current with natural latex. This is a direct result of the higher viscosity of artificial dispersions in the 50 to 60 per cent range which arises from the presence of the added hydrophilic colloid.

Artificial dispersions of rubber have been found to be more susceptible to coagulation on freezing than is natural rubber latex. The effect is not so much concerned with the temperature at which freezing takes place as with the fact that, in most cases, if the freezing has not been too severe natural latex may be gently thawed out to give a more or less unchanged fluid, whereas an artificial dispersion on thawing out will frequently be found to have coagulated. The reason is obscure, but the point should be borne in mind for the commercial handling of the material.

As might be anticipated artificial rubber dispersions are capable of being vulcanized in the same way as natural latex. A partial vulcanization, that is, a controlled heating in the presence of small quantities of zinc oxide, sulfur and ultra-accelerator, also has an apparent effect on the stability of the dispersion. The effect is not large, but probably results from the protective agents being rendered insoluble.

As mentioned previously, the nature of the dispersion depends not only on the type of dispersing agents but also on the amount. This applies particularly to the way in which the dispersion coagulates. To obtain a coherent clot on coagulation with, for example, dilute acetic acid, the colloid content should be kept to a minimum. In general, dispersions made from soap alone,

whether volatile soaps or nonvolatile soaps, give this type of coagulation if the soap content is low. Dispersions containing protein generally tend to flocculate or form weak coagula.

An interesting patent dealing with the use of a special soap has been issued[5]. This patent is concerned largely with the use of a morpholine soap. A morpholine soap, for example, morpholine oleate or morpholine stearate, is an excellent soap for dispersing purposes, and has the added advantage that the morpholine is volatile. In the example given in the patent, the only dispersing agent used for a rubber batch was 6 per cent of stearic acid and 2 per cent of morpholine on the rubber, forming morpholine stearate *in situ*. Morpholine is not so volatile as ammonia, its rate of evaporation, for example, being similar to that of water. That is, it remains in the dispersion as long as the aqueous phase is present, but at the same time it is not a fixed alkali and evaporates with the water.

Properties of films from artificial dispersions.—Just as the nature and amount of the colloid affects the properties of the dispersion itself, they also have a bearing on the nature of the dried-out or coagulated film. Films in which residual soap is present have an appreciable water absorption, so in this respect the use of a volatile soap is an advantage.

The dried-out uncured film prepared from a well masticated rubber is soft and extensible, although when cured, its physical properties approach more closely to those of a cured latex film. For example, by compounding a rubber dispersion in the usual way with sulfur, zinc oxide and an ultra-accelerator and vulcanizing the film made by drying out this compound, tensile figures of over 2.0 kg. per sq. mm. have been obtained. This is an interesting example of recovering, by ultra-accelerator action, the physical properties of a considerably masticated rubber.

Dried-out films from dispersed masticated rubber are not necessarily tacky. This depends again on the nature and amount of the colloid used. Moistening with solvent, however, even of films containing protein, imparts a greater surface tack than in the case of a latex film. The partial cure imparted by controlled heating in the presence of small amounts of vulcanizing agents results in the production of a film more closely resembling an uncured latex film in its general properties.

Synthetic latices.—A synthetic latex may be of two kinds, an artificial latex of a synthetic material made, for example, by the inversion process, or a synthetic latex made by direct emulsion polymerization.

The synthetic products of special interest are those that most closely resemble rubber and whose latices may replace natural rubber latex in various manufactures. Such materials include, for example, many of the polyvinyl compounds, butadiene-styrene rubber, Perbunan, Neoprene, organic polysulfides, Butyl rubber, polyisobutylene and the like.

Some of these have been converted to the latex form simply by dissolving in a solvent and dispersing in a colloid mill, but with the large quantity of solvent in the finished dispersion not only is the content of the synthetic product low but the use of the auxiliary solvent is wasteful and expensive.

Little can be said about the inversion of synthetic products without solvent except that it is quite feasible for such processes to be carried out. The inversion of many is not as easy as that of natural rubber, partly because many are highly resistant to water.

The dispersion of these materials is governed by the first condition that has been emphasized, namely, that the material must first of all be rendered

sufficiently plastic before an inversion process has a chance. The technique of plasticizing the various synthetics differs considerably from one to another, and its mastering is the first step in a successful process. There is still much to be learned concerning the plasticization of the various synthetic products, and as more becomes known, so the inversion process will improve.

Technically the synthetic latices occurring as the intermediate products in the manufacture of the massive synthetics are most interesting. For some, *e.g.*, butadiene-styrene rubber and Perbunan, little general experience has been gained of their latices, and some time will elapse before they are fully explored and exploited. The latices of the vinyl compounds and methacrylates have already appeared in this country. These are interesting, but they are rather specialized in their use, due partly to the nature of the finished film and partly to the rather low solids content.

Neoprene latex has been available at higher concentrations, and latices of the organic polysulfides also come in this category.

As a general rule, synthetic latices are miscible in all proportions with natural rubber latex, but in some cases exhibit abnormal behavior with respect to coagulants. A synthetic latex should approximate as closely as possible to natural rubber latex, not only in the behavior of products made from it but also in its colloid properties. As in the case of an artificial latex, it should be film-forming with coagulant, that is, the usual coagulants employed for natural latex should be capable of forming strong coherent coagula with the synthetic latex. In this way most of the processes used for natural latex can be applied directly to the synthetic latices.

In general, synthetic latices have smaller and more uniform particles than those of rubber latex. It is not clear whether this small particle size has militated in some cases against their concentration by centrifuging and creaming. There may be other reasons. There is probably a big future for synthetic latex as well as synthetic rubber, provided due attention is given to its development and that it is not treated as a byproduct. A synthetic latex stands a good chance of being more controllable in its properties than the natural product if its development is given adequate attention.

In conclusion the author's thanks are due to several of his colleagues who have carried out much of the work on which this paper is based, and to the Dunlop Rubber Co., Ltd., for permission to publish this paper.

REFERENCES

[1] Klein, British patent 296,685.
[2] Nelson, *Rubber Age* (N. Y.) **50**, 114 (1941).
[3] Baker, *Trans. Inst. Rubber Ind.* **16**, 65 (1940).
[4] Blow, British patent 541,539.
[5] British patent 539,605.

FUNTUMIA AND CEARA VS. HEVEA *

G. MARTIN

In the early days of the rubber-growing industry, when prices were high and knowledge was limited, different groups of planters pinned their faith and their money on different rubber-yielding trees such as *Funtumia elastica*, *Ficus elastica*, *Castilloa elastica*, *Manihot glaziovii* (*Ceara*) and *Hevea brasiliensis*. That the latter quickly obtained the lead over its rivals and is the sole survivor of the intervening years might be regarded as evidence that the problem is now settled, but an occasional voice in the wilderness still argues the merits of some of these other trees, particularly *Funtumia* and *Ceara*.

Hevea has now been the subject of intense study and development for over thirty years, during which time marked progress has been made in working out the best treatment to conserve the health of the tree and to produce optimum results over a long period. During this time the other trees have been neglected and the only information about their possibilities is that obtained by the early planters, who failed to make them an economic success.

There were good reasons why *Ceara* and *Funtumia* attracted attention prior to 1914, and there were also good reasons why they eventually failed to justify the faith of their protagonists. More favorable circumstances have now arisen, however, for the development of unusual sources of rubber, and the present is a unique opportunity to study their merits.

CEARA

The advantage of *Ceara*, which is of particular interest at present, is that it grows quickly and produces an abundance of seed at an early age. After about two years from planting it reaches a height approaching 15 feet and has a girth of about 15 inches at 3 feet from the ground. It can then be lightly tapped, and yields a small quantity of rubber. This compares favorably with the rate of development of *Hevea*, which is not worth tapping until over four years old, and even then yields rather soft, inferior rubber.

The *Ceara* tree therefore grows more quickly than *Hevea* during the first few years, but is smaller when mature. Another advantage of *Ceara* is that it thrives on poor soil, can withstand a reasonable period of drought and can even survive a mild frost. It can, therefore, be grown under conditions unsuitable for *Hevea*. This was a very potent argument in Ceylon, where high hopes were entertained that the tree would be particularly suitable for some parts of the Island. The argument was also a powerful one in parts of tropical Africa, particularly in East Africa.

Unfortunately, the trees growing in the drier areas do not yield freely-flowing latex, so, on tapping, the latex coagulates on the bark in the form of scrap, which has to be washed and creped. The washing of *Ceara* scrap is somewhat of an art, because of its tendency to disintegrate into large crumbs and the difficulty of obtaining a coherent sheet.

* Reprinted from the *India-Rubber Journal*, Vol. 105, No. 19, pages 464–465, November 6, 1943.

The *Ceara* tree is more difficult to tap than *Hevea*, partly because it is generally necessary to remove first a thin, hard, outer bark which damages the tapping knives and which sometimes becomes detached from the inner bark so that latex can flow between the two layers. It is also more difficult to tap because many systems of tapping are fatal. Even as late as 1914 it was reported that no system of tapping was known in Ceylon which did not involve the destruction of the tree, particularly in the dry areas. It was also suggested that this was not of great importance as the trees could be quickly replaced.

The usual method of tapping *Ceara* trees after the removal of the outer bark consists in pricking the remaining inner bark with thin-bladed knives or with ordinary prickers. In the wetter areas excision methods of tapping, in which a shaving of bark is removed, can be employed.

The yields are rather low compared with *Hevea*, and this is the chief reason why planters lost interest in *Ceara* as a source of rubber. The yield of *Ceara* plantation trees is usually between 4 and 16 ounces of dry rubber per tree per annum, but, like *Hevea*, some trees yield much more than others and single trees in East Africa have been reported to yield as much as 10 pounds. These yields are very poor compared with *Hevea*, which averages about 5 pounds per tree per annum, and some times reaches over 20 pounds. The yield per acre for *Hevea* ranges between 400 and 1,000 pounds per annum, with a density of planting of somewhat less than 100 trees per acre. The yield for *Ceara* is usually less than 200 pounds per acre, with about 300 trees per acre.

It appears, therefore, that the *Ceara* tree is more difficult to tap, is more easily damaged, and gives much smaller yields per tree and per acre than *Hevea*. The rubber is of good quality and bulk latex is easily converted into sheet with a good appearance, but it contains about 5 per cent less rubber hydrocarbon than *Hevea*. The *Ceara* tree has the war-time advantage that it can be grown quickly and tapped two years from planting. In addition, it can be grown under conditions of soil and climate unsuitable for *Hevea*.

FUNTUMIA

The *Funtumia* tree is, of course, abundant in many of the forests of tropical Africa, and it was concluded that conditions in Africa must therefore be ideal for this tree. If the wild tree can be economically tapped, how much more economical it would be to establish plantations and thus save the long, arduous and even dangerous journeys into the forest to tap widely-scattered trees. This argument was sound, but it did not allow for the fact that *Hevea* rubber could eventually become so plentiful and cheap that neither wild nor plantation *Funtumia* could compete.

It is fairly easy to establish *Funtumia* plantations, seeds are plentiful and fertile, but the trees have to be planted close together and eventually thinned out or they develop low branches which interfere with tapping. The trees do not increase in size very quickly, but the mature tree reaches a good height and girth. The bark is thin, so the tree is easily damaged by tapping. The most striking difference between *Funtumia* and *Hevea* is that the former yields most of its latex at one tapping. It does not exhibit the wound response of *Hevea*, and after the first tapping the yield rapidly diminishes unless the tree is rested for many months. That the tree only requires tapping twice a year might be an advantage if the yield per tapping is sufficiently large to reduce tapping costs compared with *Hevea*. The author has no authentic information on this point, but a normal tapping task for *Hevea* is, say, 300 trees which

altogether yield about 15 pounds of rubber per day. In the case of *Funtumia* it is necessary to make vertical and lateral incisions to a height which necessitates the use of ladders or slings and the attention of more than one laborer per tree. Since the yield of one tree is usually less than 4 ounces of dry rubber, it would be necessary for two men to tap at least 120 trees per day for tapping costs to compare with those of *Hevea*. Christie in "The African Rubber Industry", 1911, p. 182, quotes authority for the statement that the cost of planting and tapping *Funtumia* is cheaper than for any other rubber plant. When this statement was made, herring-bone tapping systems were employed for *Hevea*, and it is doubtful whether the statement is true of modern, conservative tapping systems. It is not impossible, however, with further experience to devise a more conservative tapping system for *Funtumia* which will not be more costly than that of *Hevea*, but the yield per acre per annum is not likely to exceed, say, 100 pounds, and the life of the tree is likely to be somewhat uncertain.

Funtumia latex is very stable, and this is an advantage when coagulation has to be delayed. The latex cannot be coagulated by the acids normally employed for *Hevea*. It is, therefore, coagulated by boiling which, on a large scale, is not as convenient as adding acids and may be more expensive. The rubber is of good quality, but contains about 8 per cent less rubber hydrocarbon than *Hevea*.

The *Funtumia* tree is supposed to be more resistant to disease than the *Hevea* tree in Africa, but the latter is sufficiently resistant so that this cannot be regarded as an outstanding advantage.

It appears, therefore, that *Funtumia* has an advantage over *Hevea* with regard to yield per tree per tapping. It is also less exacting regarding climate. Tapping is, however, a more difficult operation and the yield per acre is small. In addition the quality of the rubber is not quite as good.

SUMMARY

It has to be admitted that both *Ceara* and *Funtumia* have some advantages over *Hevea*. Neither is so exacting regarding climate, and *Ceara* will thrive on soil unsuitable for *Hevea*. *Ceara* has the advantage of quick growth, and *Funtumia* yields an appreciable amount of rubber per tapping per tree. On the other hand, both of them are difficult to tap, and the trees are easily damaged. The yield per acre is much less than that given by *Hevea* and the quality of the rubber produced under the best conditions is from 5 to 8 per cent inferior. The crux of the problem is to increase the yield per acre, with a corresponding reduction in tapping costs. Until this has been achieved it is difficult to believe that either tree will receive the serious attention of planters after the present emergency has disappeared.

PROCESSES OF RECLAIMING RUBBER AND THEIR RELATIVE MERITS *

E. W. B. Owen

Removal or disintegration of cellulose fibre is of great importance, and when plants do not permit of the acid or alkali processes, heat treatment has been successfully applied. Cotton can be destroyed by heating in an inert or steam atmosphere at about 260° C; but a lower temperature can be used to achieve the same object if such agents as ammonium salts are present in small quantities. To be of value, a thermal or pan process must be easily adapted to existing rubber equipment.

Thermal and pan reclaims made with such equipment have been compared with an alkali reclaim produced from the same waste taken from manufacturers' reject tires which had never seen road service and which, therefore, had a full tread. Two debeaded tires were each cut into six sections, two of which from each tire were reserved for the thermal process, and the remainder were ground and blended to the consistency used in the alkali process, and divided between the alkali and the pan processes.

The thermal process consisted in heating the unground tire sections in superheated steam at 60 lbs. per sq. in., the schedule being a 2½ hours rise to 260° C (brought about by electrical heating), one hour at 260° C, and fifteen minutes to cool with water, release it and open the pan. After this treatment the cotton was completely charred and the rubber plasticized. The product was ground and massed on a mill, and strained through a 40-mesh gauze. The temperature was taken at the door of the pan and a safety-valve working at 60 lbs. per sq. in. limited the steam pressure.

The pan process involved the addition of a charring agent and of plasticizers. Two per cent of ammonium persulfate, as a 20 per cent solution in water containing a wetting agent, served as charring agent; this was sprinkled on the waste and intimately mixed with it. Then 5 per cent of paraffin oil in which 2 per cent of coconut oil fat acid and 2 per cent of naphthalene were dissolved, was also intimately mixed with the waste. This prepared material was heated in covered pans, 4 inches deep, for three hours at 150 lbs. per sq. in. of steam (180° C) after a 15 minute rise. After drying, the product was ground and massed on a mill, mixed with 10 per cent of a high-boiling aromatic petroleum distillate termed Iranoline 2228, then strained through a 40-mesh gauze.

The alkali reclaim was kindly prepared in the laboratories of an established reclaiming company, and is presumed to have been subjected to a heat treatment of approximately 15 hours at 150 lbs. per sq. in. steam pressure in presence of the usual concentration of caustic soda. After washing and drying it would have been ground, massed, strained and refined in the normal way.

Properties of the reclaims.—Acetone, chloroform and alcoholic KOH extracts were made for 6, 4 and 4 hours, respectively. The pH was determined in 50 cc. of water in which one gram of reclaim had been boiled for one hour.

* Reprinted from the *Transactions of the Institution of the Rubber Industry*, Vol. 19, No. 3, pages 111–118, October 1943.

No positive value was obtained in analyses for the cellulose content of the reclaims. Results from each type of reclaim and from the original waste are shown in Table 1.

TABLE 1

ANALYSIS

	Original waste	Alkali reclaim	Thermal reclaim	Pan reclaim
Acetone extract	7.0	11.1	7.2	19.5
Chloroform extract	0.9	19.1	15.3	13.0
Alcoholic KOH extract	3.5	3.9	3.3	6.4
Free carbon	17.8	9.6	24.5	15.0
Ash	8.4	16.0	10.7	8.3
Cellulose	18.4	...	...	...
Rubber (calculated)	44.0	59.4	55.3	50.8
pH	...	9.8	7.0	7.0

From the chloroform extracts it appears that the degree of depolymerization attained in the three processes is of the same order, although possibly a little higher in the case of the alkali reclaim. Variation in the carbon contents may be understood when it is realized that in the thermal process the cotton is thoroughly carbonized, whereas charring proceeds to an intermediate scorched product (possibly accounting for the increase in alcoholic KOH extract) in the pan process. The markedly low free carbon in the alkali reclaim can be attributed to an incomplete reclaiming of the waste; with the pan reclaim this is slight, but with the alkali reclaim it is more serious. Incompletely reclaimed particles removed in the straining and refining processes are from the tread part of the waste. This is confirmed by the high ash of the alkali reclaim. Some of the most valuable part of the waste is extracted in the tailings when refining alkali reclaim and has to be reprocessed. High acetone extract indicates the presence of softener in the pan and alkali reclaims, as also would the chloroform extract of the latter if the softener were mineral rubber. The higher pH value of the alkali reclaim was expected.

Specific gravities were determined on reclaim-sulfur mixes. Properties of these mixes are recorded in Table 2. Tensile strengths are expressed in kg. per sq. cm.; the elongations in percentage.

TABLE 2

PROPERTIES OF 95-RECLAIM-5-SULFUR MIXES

Time of cure at 287° F (min.)	20	30	40
Alkali			
Tensile strength	58.5	52.0	44.9
Elongation at break	380	305	205
Hardness (Shore)	56	58	62
Sp. gr. of mix	1.182	...	...
Sp. gr. of reclaim	1.15	...	...
Thermal			
Tensile strength	22.7	26.6	32.3
Elongation at break	340	325	280
Hardness (Shore)	44	48	52
Sp. gr. of mix	1.205	...	...
Sp. gr. of reclaim	1.18	...	...
Pan			
Tensile strength	53.3	47.5	43.6
Elongation at break	377	307	277
Hardness (Shore)	54	59	59
Sp. gr. of mix	1.185	...	...
Sp. gr. of reclaim	1.16	...	...

Differences in rate of cure and physical properties will be noted, although specific gravities are comparable. The pan reclaim was little inferior to the alkali type, but the thermal reclaim was much lower both in rate of cure and properties. It should be emphasized that results obtained with rubber-sulfur mixes are no criterion of the behavior of these materials in a practical compound.

The properties of a tread-type compound in which each of these reclaims was present in a proportion equal to that of the natural rubber was next examined. For acceleration, mercaptobenzothiazole (MBT) was used in one set of tests, and a butyraldehydeaniline condensation product (BA) in another.

TEST COMPOUND (TREAD TYPE)

Smoked sheet rubber	65
Reclaim	65
Zinc oxide	5
Stearic acid	2
Sulfur	3
Accelerator	0.5
Carbon black	35

Antioxidant was omitted so as to obtain aging results more rapidly. The total rubber hydrocarbon in this formula was considered as 100 parts by weight. Laboratory batches were prepared under uniform conditions of time and temperature in an internal mixer, and after 16 hours' rest, were cured for 10, 20, 30 and 40 minutes at 307° F. At the same time plasticities were determined; conditions of the test and the results obtained are shown in Table 3.

TABLE 3

PLASTICITIES (at 100° C)

Dimensions of pellet: 1 sq. cm. cross-section, 1 cm. high.
Preheat of 15 min. at 100° C, 16 hours after mixing.
Plasticities expressed as time in seconds for compression from 8 mm. to 6 mm. under a load of 1,000 g.

	Accelerator	
	BA	MBT
Alkali reclaim	100	67
Thermal reclaim	37	25
Pan reclaim	18	12

TABLE 4

PHYSICAL PROPERTIES

Alkali Reclaim Stocks

Unaged	MBT accelerated				BA accelerated			
Cure at 307° F (min.)	10	20	30	40	10	20	30	40
Tensile strength	196	193	178	169	192	191	185	178
Elongation at break	520	460	450	450	550	470	460	450
Modulus at 300 per cent	96	109	111	115	85	105	111	117
Permanent set	24	22	18	17	23	24	24	22
After aging for 120 *hours at* 80° C								
Tensile strength	184	169	153	136	176	164	152	132
Elongation at break	470	400	350	310	480	410	380	350
Modulus at 300 per cent	107	118	114	110	108	132	128	106

It will be noted that the stocks containing MBT were softer than the respective stocks employing BA to exactly the same extent and, furthermore, the two new types of reclaim gave softer stocks than the alkali reclaim.

Tensile properties of the cured alkali reclaim stocks are shown in Table 4.

Contrary to expectation, the BA stock gave a flatter cure than the MBT stock. Optimum tensile strength was already attained at the 10 minute cure. Only slight differences existed between the unaged stocks. When aged, the BA stock tended to remain more elastic but deteriorated in strength more than the MBT stock, especially with increasing overcure.

It can be seen from Table 5 that there was a decided difference in the rates of cure of the thermal reclaim stocks, whereas with the MBT stock 10 minutes

TABLE 5

PHYSICAL PROPERTIES

Thermal Reclaim Stocks

Unaged	MBT accelerated				BA accelerated			
Cure at 307° F (min.)	10	20	30	40	10	20	30	40
Tensile strength	155	155	150	135	112	125	143	153
Elongation at break	550	475	460	450	500	490	470	460
Modulus at 300 per cent	76	89	98	104	65	75	84	95
Permanent set	20	22	22	24	22	22	18	20
After aging for 120 *hours at* 80° C								
Tensile strength	154	147	139	129	104	116	128	134
Elongation at break	450	360	330	310	440	350	330	310
Modulus at 300 per cent	99	120	118	105	74	98	103	107

gave optimum tensile strength, 40 minutes was required with the BA stock which was then less elastic and more susceptible to aging.

The decrease in tensile strength of the MBT stock was noticably small.

In the case of the pan reclaim stocks it will be observed in Table 6 that these two accelerators showed their usual characteristics, *i.e.*, MBT produced a flat cure and BA a peak cure.

TABLE 6

PHYSICAL PROPERTIES

Pan Reclaim Stocks

Unaged	MBT accelerated				BA accelerated			
Cure at 307° F (min.)	10	20	30	40	10	20	30	40
Tensile strength	185	185	180	170	172	183	175	163
Elongation at break	550	510	500	490	550	520	480	470
Modulus at 300 per cent	71	83	88	89	69	82	88	94
Permanent set	16	18	18	18	19	20	22	20
After aging for 120 *hours at* 80° C								
Tensile strength	163	162	150	142	131	134	127	117
Elongation at break	450	400	380	370	460	390	340	320
Modulus at 300 per cent	97	112	112	102	74	101	113	104

Here again the BA stock was slower curing than the MBT stock. Optimum properties were similar for each, and again the effect of aging was to produce a greater deterioration of the BA stock.

Optimum properties of the various stocks are compared in Table 7.

TABLE 7

OPTIMUM PROPERTIES

Stock	Before aging				After aging		
	Cure (min.)	T_B	E_B	T_{300}	T_B	E_B	T_{300}
Alkali/MBT	10	196	520	96	184	470	107
Alkali/BA	10	192	550	85	176	480	108
Thermal/MBT	10	155	550	76	154	450	99
Thermal/BA	40	153	460	95	134	310	107
Pan/MBT	10	185	550	71	163	450	97
Pan/BA	20	183	520	82	134	390	101

The following conclusions are drawn:

(1) Alkali reclaim stocks give the best tensile strengths. Pan reclaim stocks give tensile strengths only 5 per cent lower, and thermal reclaim stocks about 20 per cent lower. Elongations at break are, with one exception (thermal/BA stock), comparable.

(2) BA is not suited to the thermal and pan stocks because of retarded cure and poor aging, compared with MBT. Greatest tensile strength degradation with MBT is less than 12 per cent, whereas with BA it amounts to 27 per cent.

(3) MBT gives rise to stocks possessing better elongations at break after aging.

(4) Thermal and pan stocks with MBT are not so stiff as corresponding alkali stock before aging. After aging, however, modulus results are of the same order, although those of thermal and pan stocks are slightly below the average.

Further properties at optimum cure are shown in Table 8. Permanent set was determined after stretching for ten minutes at 300 per cent elongation

TABLE 8

Stock	Permanent set	Hardness (Shore)	Abrasion loss
Alkali/MBT	24	60–61	3.43
Alkali/BA	23	58	3.35
Thermal/MBT	20	55	3.15
Thermal/BA	20	58–59	3.27
Pan/MBT	16	60–61	2.55
Pan/BA	20	60–61	2.69

and 10 minutes' rest after release. The abrasion loss is expressed in percentage weight lost for 1000 revolutions of the abrasive wheel; an Akron Standard Mold Co. machine set at 15° was used for this determination.

Both thermal and pan reclaim stocks were better in permanent set and abrasion resistance than the standard. In the latter property the losses were 92 per cent and 74 per cent of that of the standard, for the thermal and pan/MBT stocks, respectively. Shore hardness figures were, with one exception, near 60° C. That exception, the thermal/MBT stock, had other characteristics: it was the only optimum cured MBT stock which bloomed, and had the lowest tensile strength of the MBT stocks. It was felt that a modification of accelerator might prove advantageous. Tetramethylthiuram disulfide, to the extent of 20 per cent of the MBT content, was therefore added to this stock and further tests made (Table 9).

TABLE 9

PHYSICAL PROPERTIES

Thermal Reclaim Stocks

Unaged	MBT-Tuads accelerated				
Cure at 307° F (min.)	5	10	20	30	40
Tensile strength	163	159	156	150	146
Elongation at break	630	560	530	520	510
Modulus at 300 per cent	50	62	69	71	71
Permanent set	18	16	20	20	20
After aging for 120 *hours at* 80° C					
Tensile strength	164	158	140	133	120
Elongation at break	490	450	390	370	360
Modulus at 300 per cent	89	103	107	105	104

Although there was an increase in rate of cure, with the disadvantage of quicker set-up, there was an increase in tensile strength, a decrease in modulus and a very marked increase in the elongation at break—the best obtained. The tensile strength was only 15 per cent below that of the alkali/MBT stock.

The manufacturers of reclaim are very emphatic as to the important part which refining plays in their processes. The effect of this operation on the products of the thermal and pan processes described is shown in the properties of their respective MBT stocks in Table 10.

TABLE 10

PHYSICAL PROPERTIES

Refined Reclaim Stocks

Unaged	Thermal/MBT				Pan/MBT			
Cure at 307° F (min.)	10	20	30	40	10	20	30	40
Tensile strength	147	155	152	142	182	187	175	169
Elongation at break	600	550	520	480	590	550	520	500
Modulus at 300 per cent	58	73	75	78	63	78	82	83

It came as a surprise to find that this extra mechanical treatment did not improve the tensile strength of either reclaim. There was a decrease in the modulus of the cured stock and a decided slowing of the cure. It would appear that the effects of refining on tensile strength have been overrated in so far as these particular processes are concerned.

One other comparison was made: the MBT stocks were formed into a tube by extrusion. The percentage increase in diameter over that of the die was noted. The expansions were 26.5 per cent, 9.5 per cent and 18.5 per cent for the alkali, thermal and pan stocks, respectively. The alkali and pan stocks gave a slightly rough extrusion while the thermal stock gave a smooth finish; but the tube sagged in the cure.

SUMMARY

1. A more complete reclamation is possible by the thermal and pan process than with the alkali process, and both the former effect a saving in time.

2. The thermal process calls for a higher temperature, but the after-treatment consumes less power for grinding. The pan process makes use of a lower temperature; but the expenditure of more power for grinding before and after treatment, as well as a drying period, are entailed.

3. The new products are neutral, and softer than alkali reclaim.

4. Accelerated with BA, stocks with these new types of reclaim give poor results. On the other hand, MBT offers good prospects, both for aging and acceleration.

5. Whether refined or not, the pan reclaim produced a tensile strength 95 per cent of alkali reclaim, and the thermal reclaim 80 per cent, in MBT stocks.

6. With modified acceleration, thermal reclaim stock can be made to give improved tensile properties.

7. Laboratory abrasion resistance of both new types was superior to the standard, the losses being 92 per cent and 74 per cent for thermal and pan reclaims, respectively.

8. The permanent set was lower despite the softener in the pan reclaim.

9. Despite the lack of refining, articles formed by extrusion from stocks containing thermal and pan reclaims compared favorably with those from alkali reclaim with regard to surface finish.

10. Thermal reclaim ages extremely well.

Independent workers in the field of thermal reclaim have been able to exercise a finer control of the process, and a large scale plant is in course of erection as a result of the improvements effected.

Further work is proceeding, and it is hoped that a product superior in all respects to alkali reclaim will be obtained.

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